CHEMICAL PROCESS DESIGN

A SYMPOSIUM

Council of Scientific & Industrial Research
New Delhi

CHEMICAL PROCESS DESIGN

Chemical industry in India has entered a new phase in the Third Plan. 'Basic manufacture' and 'local skill' are the pass words for the industry during the period. Taking cognizance of the importance of process development and design of equipment by Indian personnel in this context, a symposium on chemical process design was organized by the Chemical Research Committee of CSIR. The papers presented and discussed in this symposium are included in this publication, grouped under the heads: Chemical Process Development, Chemical Process Equipment and Operating Experiences of Chemical Production Plants. Whether you are a chemist, a chemical engineer or a chemical technologist—in research or industry—you will find enough material to give you an idea of the advances made and the problems awaiting solution in your field of interest.

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A Symposium

Held under the auspices of
Chemical Research Committee, CSIR: July 24-25, 1961
at the Department of Chemical Engineering
Indian Institute of Science, Bangalore

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PREFACE

The Chemical Research Committee of the Council of Scientific & Industrial Research, under the chairmanship of late Prof. B. C. Guha, decided at its meeting held in Allahabad in January 1961 that a symposium on Chemical Process Design should be held in July 1961 at the Department of Chemical Engineering, Indian Institute of Science, Bangalore. The Committee felt that there was an urgent need to develop indigenous 'know-how' for the manufacture of various chemicals which are to be produced in the country as imported know-how is bound to be old and obsolete and dependence on such know-how will place Indian manufacturers in a disadvantageous position in the competitive world markets. It was also felt that a symposium of this nature would provide an opportunity for research workers from various laboratories to discuss the utilization of research results with personnel from industry and similarly for industrial personnel to discuss their research needs with laboratory workers.

Though the notice given to submit papers was short, the response was, on the whole, encouraging, and the symposium proved to be a great success inasmuch as it attracted a large number of delegates from various industrial units and research laboratories, and enthusiastic discussions took place on each of the papers presented.

The present publication includes most of the papers read at the symposium. The papers have been grouped under the following heads: (i) Chemical Process Development; (ii) Chemical Process Equipment Design; and (iii) Operating Experiences of Chemical Production Plants. Scaling up of chemical process was one of the topics proposed for discussion but unfortunately no suitable papers were received under this group.

N. R. KULOOR
Convener

CONTENTS

PAGE

PREFACE v

CHEMICAL PROCESS DEVELOPMENT

Production of Hexachlorobenzene from Monochlorobenzene .. 1
P. R. BISHNOI, M. M. SHARMA & K. H. SHAH

Development of a Manufacturing Process for Bisphenol A .. 7
S. S. MUKHOPADHYAY & A. N. SAHA

Design of Reactor for Manufacture of Trichloroacetic Acid from Chloral Hydrate 10
D. D. DESHPANDE & R. SUNDARAM

Concentration of Rectified Spirit using Solid Desiccants .. 16
B. VENUGOPAL, S. H. IBRAHIM & N. R. KULOOR

Development of HMX for Utilization in Powerful Explosives .. 22
D. B. PARIHAR, K. K. SHUKLA, P. K. SAXENA & K. R. D. CHANDIRAMANI

Design Considerations for a Reactor for Chemical Exchange Method of Producing Heavy Water 32
C. V. KALYANASUNDARAM, R. KUMAR & R. L. DATTA

Studies on Extraction of Uranium, Niobium and Tantalum from Samarskite 36
T. R. BHAT, Y. W. GOKHALE, B. S. MATHUR & V. S. SASTRY

Preparation of Pectolytic Enzymes 47
M. H. BILIMORIA

Kinetics of Coal Carbonization in Fluidized State 58
P. SEN GUPTA, K. J. R. SARMA, P. SEN & M. N. RAO

Plant for Manufacture of Potassium Chlorate 94
S. RAMASWAMY & N. KALYANAM

CHEMICAL PROCESS EQUIPMENT DESIGN

Some Aspects of Fractionating Tray Design and Selection .. 97

PAGE

Separation by Sweep Distillation 111
M. Subramaniam, R. Kumar & R. L. Datta

Prediction of Local Plate Efficiency 125
G. Narasimhan

Estimation of Hold-up in Packed Liquid-Liquid Extraction Columns at and below Flooding 129
P. Chandrasekharan & G. S. Laddha

Application of Corrosion-resistant Nickel, Nickel Alloys and Stainless Steels in Chemical Industry 138
P. N. Gandhi

Design Problems in Corrosion Engineering 153
J. Sundararajan & T. L. Rama Char

Centrifugal Thin Film Processing Units 160
K. S. Gokhale

An Experimental Thin Layer Evaporator 167
V. Subrahmanyan, B. S. Ramachandra, J. I. D'Mello, M. N. Vasudev Rao, P. K. Ramanathan, S. S. Kalbag, S. K. Lakshminarayana & B. H. Krishna

Process Design of a Fluidized Bed Reactor for Producing Phthalic Anhydride from Naphthalene 171
N. A. Mohan Rao

Some Important Aspects of Fluid Beds 180
R. Satapathy

OPERATING EXPERIENCE OF CHEMICAL PRODUCTION PLANTS

Use of some basic Heat Transfer Concepts in stepping up Production from a Sulphuric Acid Plant 185
Rajeshwar Kumar Gupta & Sh. Satyabrat Kar Chaudhuri

Work Efficiency in Alcohol Distillation 191
J. P. Kapur & V. R. Pabbi

Author Index 199

Production of Hexachlorobenzene from Monochlorobenzene

P. R. BISHNOI, M. M. SHARMA & K. H. SHAH
Department of Chemical Technology, University of Bombay, Bombay

Optimum conditions for the production of hexachlorobenzene in maximum yields by the chlorination of monochlorobenzene have been established as a result of a study of such factors as type and concentration of catalyst, temperature and duration of reaction and rate of chlorination. On the basis of data obtained from bench pilot plant experiments with 2 kg. of monochlorobenzene, recommendations have been made for the setting up of a plant of capacity, 1 tonne/day. Economics of the process with particular reference to the recovery of by-products have also been discussed.

Chlorinated products of benzene have a wide variety of uses either as such or as starting points for making industrial chemicals. For example, trichlorobenzenes are used as components of mixtures for insulating materials and as solvent for making dyes and pigments. 1, 2, 4, 5-Tetrachlorobenzene is an intermediate for the production of 2, 4, 5-trichlorophenol; hexachlorobenzene finds its main use as an intermediate for making pentachlorophenol, which is largely used as wood preservative.

The results of investigation on the production of hexachlorobenzene from monochlorobenzene are presented in this paper.

The process for making monochlorobenzene from benzene is well established and already two plants are working in this country. Monochlorobenzene is comparatively easy to handle and store. Hence, investigations were undertaken to study the chlorination of monochlorobenzene. The reaction can be expressed as follows:

$$C_6H_5Cl\ (l) + 5Cl_2\ (g) \rightleftharpoons C_6Cl_6(s) + 5HCl\ (g)$$

$$\triangle F = -151{\cdot}005 \text{ k.cal./gram mole at } 25^\circ C.$$

$$\triangle H = -144{\cdot}115 \text{ k.cal./gram mole at } 25^\circ C.$$

The reaction is thermodynamically highly feasible and roughly 30 k. cal. of heat are evolved for every gram mole of chlorine reacted. From this it is clear that adequate provision for the control of temperature of the reactor has to be made. Also, some of the polychlorobenzenes have a marked tendency to sublime with the result that difficulty may be encountered in the operation of the reactor. Experiments were conducted keeping these two points in view.

EXPERIMENTAL DATA AND RESULTS

The glass equipment set up for the chlorination is shown in Fig. 1. Using this, the effects of such factors as type and quantity of catalyst, rate of chlorination, temperature and duration of chlorination were studied.

First, the temperature was fixed at 120°C. and the rate of passage of chlorine at 1·05 mole/mole of chlorobenzene/hr. Different types and quantities of catalysts were used for chlorination. From the results, recorded in Table 1, it can be seen that ferric chloride (0·10 per cent) is quite satisfactory for carrying out the reaction.

Next, keeping the quantity of ferric chloride at 0·1 per cent and the temperature at 120°C., the rate of chlorination was varied from 0·88 to 1·47 mole/mole of chlorobenzene/hr. The results of these trials are represented in Fig. 2.

With a view to studying the effect of temperature, the experiment was carried out in two stages. In the first stage, monochlorobenzene was chlorinated at 120°C. at 1·05 moles of chlorine/mole of chlorobenzene/hr. Chlorination was continued till the specific gravity reached a value between

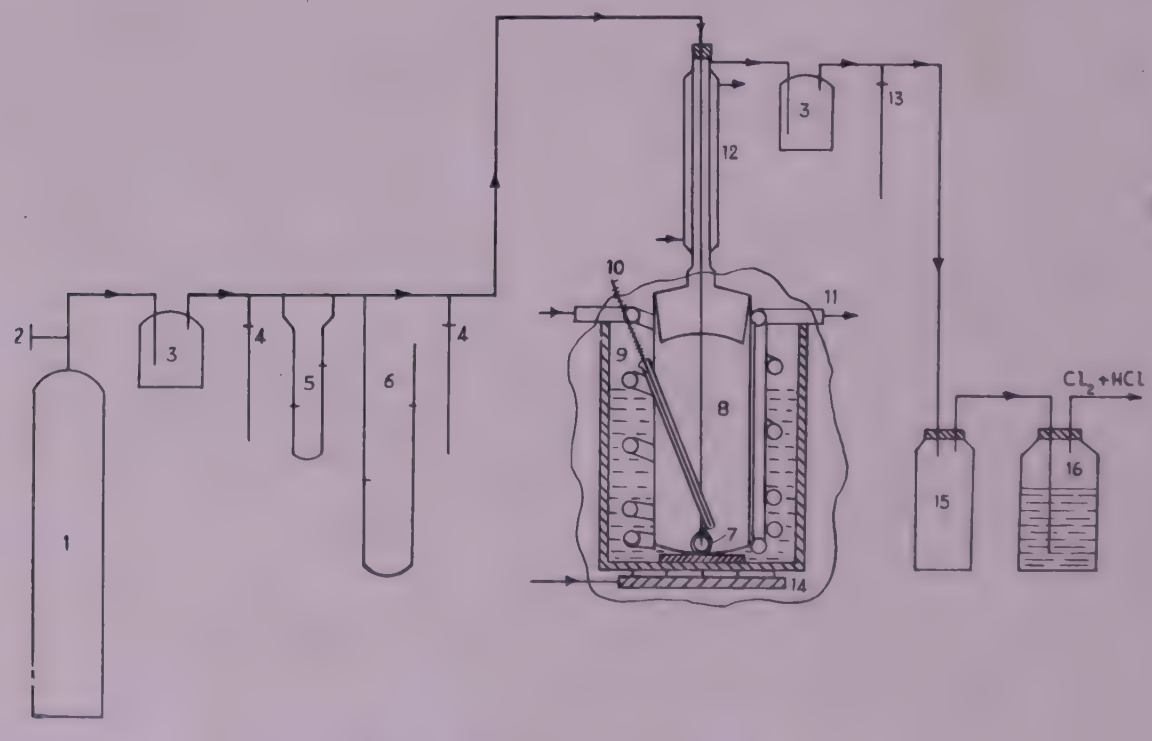

FIG. 1—CHLORINATION SET-UP

(1) CHLORINE CYLINDER ; (2) VALVE ; (3) SEPERATOR ; (4) CHECK VALVE ; (5) FLOW METER ; (6) MANOMETER ; (7) GAS DISTRIBUTOR ; (8) REACTOR ; (9) OIL BATH ; (10) THERMOMETER ; (11) HELICAL COIL ; (12) CONDENSER ; (13) GAS SAMPLE ; (14) GAS BURNER ; (15) TRAP ; (16) SCRUBBER

TABLE 1 EFFECT OF TYPE AND AMOUNT OF CATALYST ON CHLORINATION OF MONOCHLOROBENZENE

[*Charge (monochlorobenzene)*, 175 *g.* (1·55 *gram mole*); *temp.*, 120°*C.*; *rate of chlorine*, 1·05 *mole/mole of monochlorobenzene/hr*]

Catalyst	Concn of* catalyst %	Time† *min.*	Sp. gr. range (*hexachlorobenzene*)
Nil	Nil	125	1·157–1·204
Electrolytic iron powder	1·0	150	1·60 –1·65
$FeCl_3$	1·0	170	1·60 –1·65
$SbCl_3$	1·0	215	1·60 –1·65
I_2	1·0	160	1·35 –1·40
Iron powder+I_2	0·9 0·1	165	1·60 –1·65
$SbCl_5$	1·0	170	1·60 –1·65
$FeCl_3$+$POCl_3$	0·9 0·1	176	1·60 –1·65
$AlCl_3$+NaCl	1·0 0·1	175	1·40 –1·45
$FeCl_3$	0·498	170	1·60 –1·65
$FeCl_3$	0·2061	170	1·60 –1·65
$FeCl_3$	0·1	170	1·60 –1·65
$FeCl_3$	0·0474	183	1·60 –1·65
$FeCl_3$	0·01315	225	1·55 –1·60

*Percentage of anhydrous salts on the basis of monochlorobenzene charged
†Time taken to obtain the specific gravity reported

1·55 and 1·60. The reaction product thus obtained was chlorinated further at 160°, 180° and 200°C., keeping other variables the same as those employed in the first stage. The results obtained in the second stage of each experiment are shown in Fig. 3.

During the course of the experiments, it was observed that the tendency of the polychlorobenzenes to sublime increased markedly with increase in either the temperature or the extent of chlorination. Consequently, chlorination has to be carried out first up to a predetermined level and then in a second stage, the temperature of chlorination is kept as low as possible but high enough to maintain the final product in a liquid state.

The rate of chlorination under a set of conditions may, in addition, depend upon the mode of distribution of chlorine and the geometry of the reactor. Hence, bench pilot plant experiments were carried out by taking

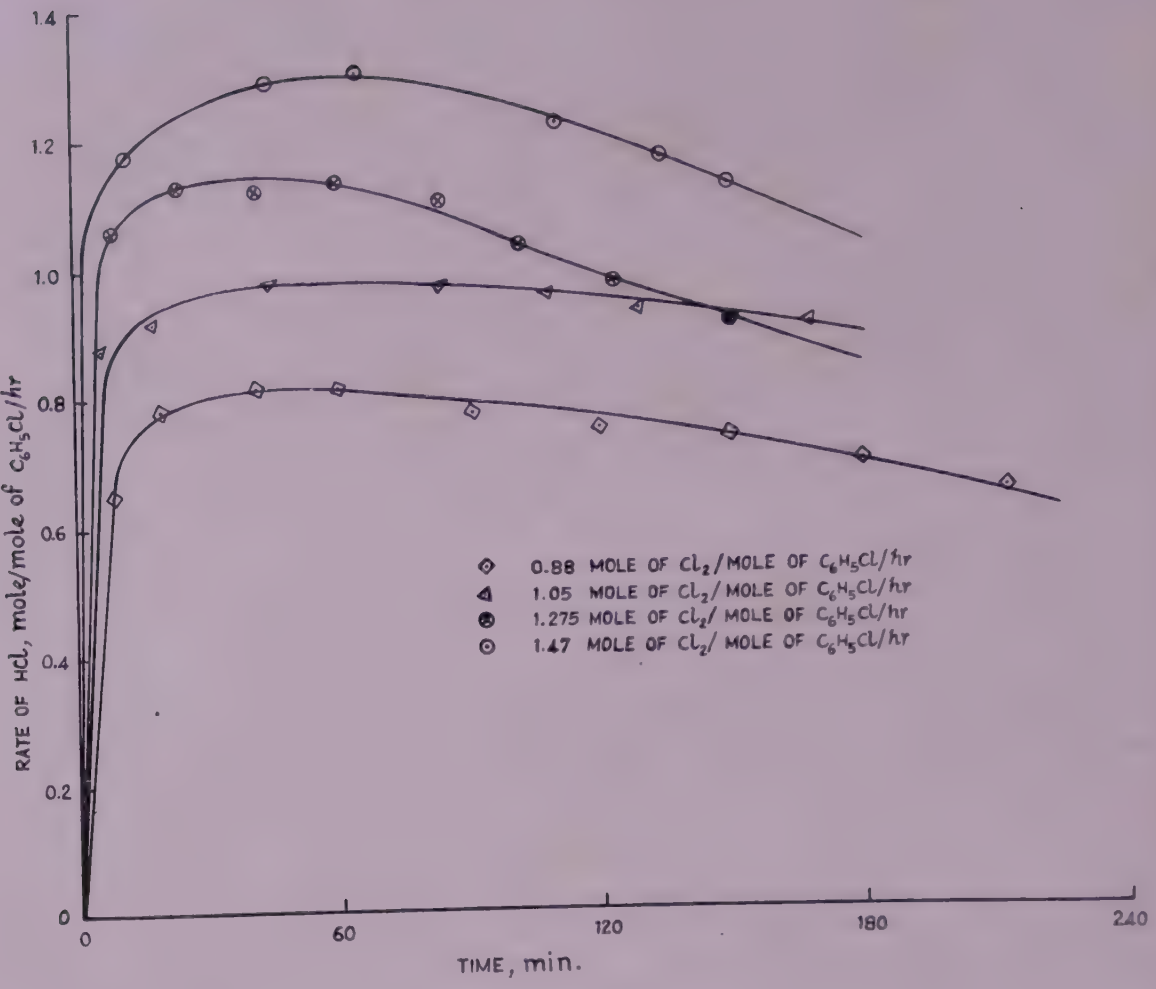

FIG. 2—VARIATION OF RATE OF HCl EVOLUTION WITH TIME AT DIFFERENT RATES OF CHLORINATION

c. 2 kg. of monochlorobenzene in a reactor made of mild steel having an internal diameter of *c.* 10 cm. The reactor was provided with an inlet for gas, a thermometer pocket and a condenser. The distributor attached to the inlet of gas was made of steel cup wrapped with mild steel wire gauze. The set-up was very similar to that used with the glass reactor. The chlorination was carried out at the rate of 0·75 mole/mole chlorobenzene/hr at 120°C. No chlorine came out unreacted. It was also concluded that agitation of the reactants should be provided for in the industrial reactor in order to avoid localized reaction and that efficient cooling should be provided for dissipating the heat of reaction.

The scheme suggested for the manufacture of hexachlorobenzene is shown in Fig. 4. In the first reactor, the chlorination is done at 120°C. till the product attains a specific gravity between 1·45 and 1·5. If intermediary polychlorobenzene compounds are desired, the product may be subjected to fractional distillation. In the second reactor, the chlorination is carried out at 160°C. till the product attains a specific gravity between 1·85 and 1·90.

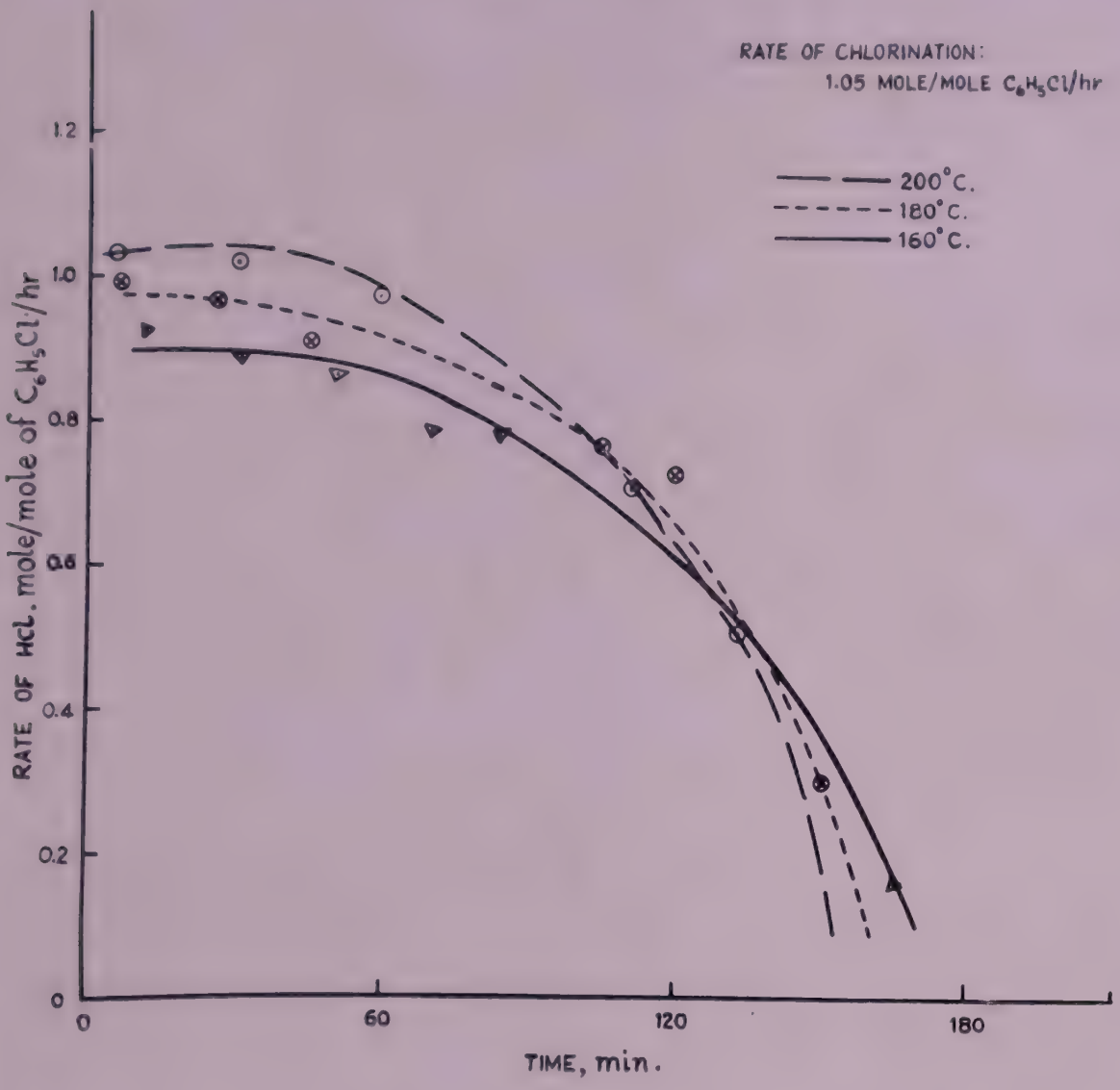

FIG. 3—VARIATION OF RATE OF HCl EVOLUTION WITH TIME AT DIFFERENT TEMPERATURES

At this stage, the reaction product contains about 30 per cent (w/w) hexachlorobenzene and remains in the liquid condition at the temperature of chlorination. Hexachlorobenzene can be separated from the product by cooling to about 100°C., when it separates out in a crystalline condition. The slurry is centrifuged to separate the crystals and the mother liquor recycled.

The capital investment (excluding steam generation unit) works out to *c.* Rs 3 lakhs which includes working capital of about Rs 90,000. The land requirements are *c.* 1700 sq. m., the actual built-up area being roughly 200 sq. m. Utilities required are process water, power and steam.

It is strongly recommended that the production of this material should be taken up by an electrolytic caustic soda manufacturer in which case the capital investment as well as the production cost will be lowered. It is also

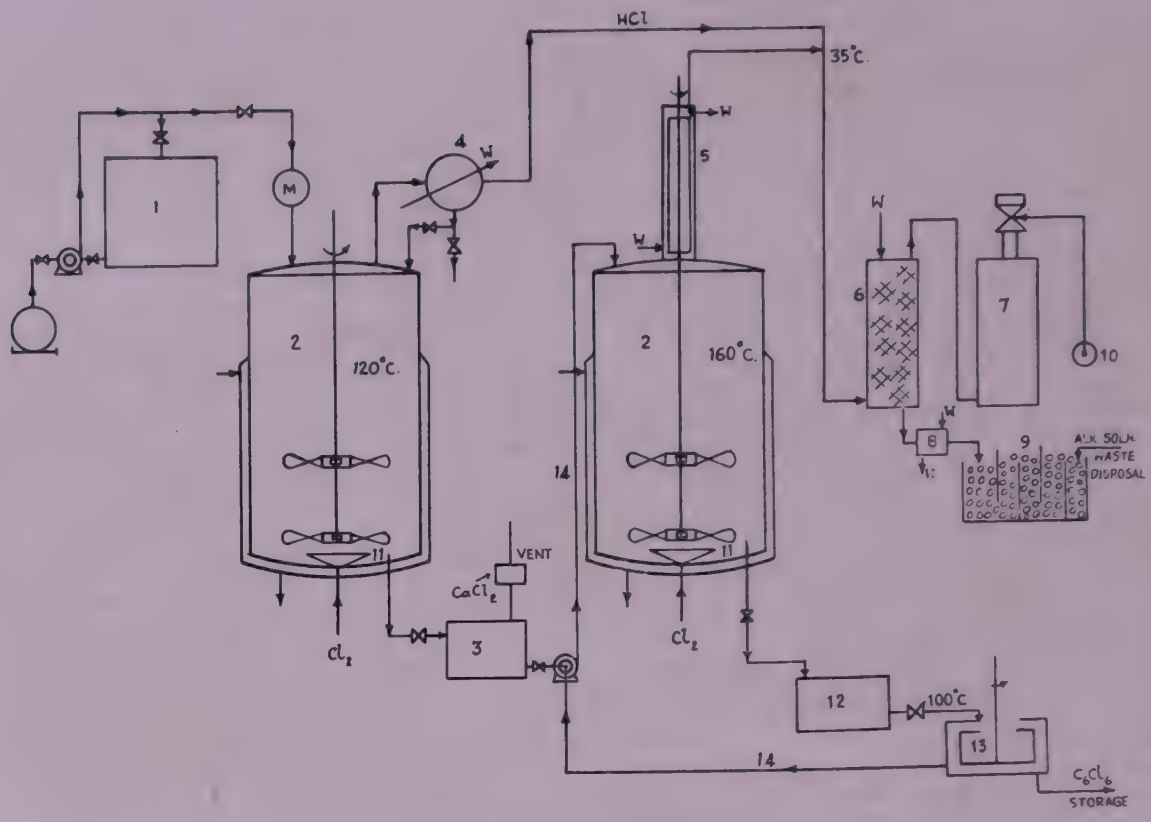

FIG. 4—PROCESS FLOWSHEET:

(1) C_6H_5Cl STORAGE; (2) CHLORINATOR; (3) $C_6H_3Cl_3$ STORAGE; (4) CONDENSER; (5) SCRAPPER CONDENSER; (6) ABSORBER; (7) FUME DISPOSAL TOWER; (8) COOLER; (9) NEUTRALIZER; (10) FLOWER; (11) SPARGER; (12) CRYSTALLIZER; (13) CENTRIFUGE; (14) STEAM-HEATED PIPE

suggested that the production of monochlorobenzene be also undertaken by the same company. The production of this chemical can also be taken up in India by the two factories producing DDT under the Hindustan Insecticides Ltd.

Development of a Manufacturing Process for Bisphenol A

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University College of Science & Technology, Calcutta

A process for the manufacture of Bisphenol A — a condensation product of phenol and acetone — has been studied using an ionizable sulphur compound as catalyst for the condensation. The effect of various factors, such as phenol-acetone ratio, temperature and concentration of catalyst, on the yield has also been studied.

Bisphenol A is a condensation product of phenol and acetone. Its importance has increased on account of its use in epoxy resins. Though it is one of the important commercial petrochemicals, information about its production in terms of process variables, reaction conditions, etc. is very meagre. The little which is available is shrouded in the patent literature.

In the patented processes, different types of condensing agents and catalysts in either the presence or absence of solvent have been used.

Anhydrous hydrochloric acid[1] was first used as a condensing agent in the absence of any solvent. With concentrated acid[2] the time of condensation was prolonged (2 days to 20 weeks as against 4 to 8 hr) and only an impure product was obtained. Instead of hydrochloric acid, sulphuric acid[3] was used in the presence of halogenated hydrocarbon solvents but without any improvement.

A mixture of hydrochloric and hydrochromic acids[4] was also tried but found to be no more efficient than anhydrous hydrochloric acid alone.

Addition, as catalyst, of mercapto substituted aliphatic carboxylic acid to the acid medium shortened the time of reaction and increased the yield.

Low molecular weight mercaptans[5] were found to be suitable catalysts in this condensation reaction. Of these, methyl mercaptan in concentrations of 0·1–1·0 per cent was the most effective.

The results of experiments using an ionizable sulphur compound as a catalyst and dry hydrogen chloride as the condensing agent are recorded in this paper.

EXPERIMENTAL PROCEDURE AND RESULTS

A definite amount of the catalyst was dissolved in a mixture of phenol and acetone in a reactor and dry hydrogen chloride gas was passed at the

rate of 100 ml./hr till the mass became semi-solid. The reactor was maintained at constant temperature. Part of the acetone was carried away with hydrogen chloride. The amount lost by this way could not be estimated. The reaction mass was washed with hot water. The wash water contained unreacted phenol, which was estimated iodometrically. The melting point of the water-washed samples was determined. Table 1 records the results.

It is evident from Table 1 that with the increase of catalyst concentration the yield also increases and that after a certain concentration there is no further improvement in the yield.

In the next series of experiments the ingredient ratio was varied while the other parameters were fixed.

It is clear from Table 2 that the higher the molar ratio of phenol to acetone, the higher is the yield.

In the third series of experiments, the molar ratio, duration of reaction and catalyst concentration were maintained as in the second experiment,

TABLE 1—EFFECT OF CATALYST CONCENTRATION ON YIELD OF BISPHENOL A

(*Molar ratio of phenol to acetone*, 2: 1; *temp.*, 55°C.; *duration*, 2·5 *hr*)

Conc. of catalyst %	Yield* %	M.P. °C.
0·29	36·3	152
0·46	45·6	149
0·64	50·0	150
0·72	52·8	148
0·80	52·8	148

*On the basis of phenol

TABLE 2—EFFECT OF RATIO OF INGREDIENTS ON YIELD OF BISPHENOL A

(*Temp.*, 55°C.; *duration*, 2·5 *hr*; *catalyst conc.*, 0·72%)

Molar ratio of phenol: acetone	Yield %	M.P. °C.
2:1	52·8	148
1·5:1	42·3	146
1:1	33·0	147

TABLE 3—EFFECT OF TEMPERATURE ON YIELD OF BISPHENOL A

(Molar ratio of phenol to acetone, 2 : 1; duration, 2·5 hr; catalyst conc., 0·72%)

Temperature °C.	Yield %	M.P. °C.
55	52·8	148
45	57·0	145
40	60·0	148
35	60 0	148

TABLE 4—RELATIONSHIP BETWEEN YIELD, MELTING POINT AND COLOUR OF BISPHENOL A

Yield %	M.P. °C.	Colour of sample
33·0	147	Tan
36·8	152	Light tan
42·3	146	Tan
50·0	150	Tan
52·8	148	Yellowish
57·0	145	Light tan
60·0	147	Yellowish

but the temperature was varied. The results are recorded in Table 3. From the table it can be seen that with the lowering of temperature the yield increases by about ten per cent and that the average room temperature is quite suitable for the purpose. The colour of the product and the melting point seem to have no regular relationship (Table 4). Neither are they related with the yield.

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Design of Reactor for Manufacture of Trichoroacetic Acid from Chloral Hydrate

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Optimum conditions for the best yields of trichloroacetic acid by the oxidation of chloral hydrate with concentrated nitric acid have been established. Eighty per cent conversion is obtainable at 60°C. with an oxidation time of 6 hr and the molecular ratio of $CCl_3CH(OH)_2$: HNO_3 as 1: 2. Based on these data, design calculations have been presented for a reactor producing 250 kg. of trichloroacetic acid.

Trichloroacetic acid is not at present manufactured in India but considering its uses in the production of medicinals[1-6] and in the polymerization of formaldehyde[7] and styrene, it is likely to find a ready market. Oxidation of chloral is the most convenient process for the manufacture of trichloroacetic acid. Chloral is readily available in India from the two DDT plants which have already been working.

Air oxidation of chloral vapour would be the cheapest process for the production of trichloroacetic acid. The reaction is, however, extremely slow and many side reactions which will adversely affect the yield of trichloroacetic acid are possible. A detailed thermodynamic study of the vapour phase oxidation of chloral showed that all the side reactions, in addition to the main reaction $CCl_3CHO \xrightarrow{(O)} CCl_3COOH$, are equally probable. At high temperatures, the decomposition of trichloroacetic acid is also unavoidable. The results also indicate the necessity of carrying out the oxidation at as low a temperature as possible to get good yields. Since chloral hydrate is more stable than chloral, it can conveniently be used as the starting material and hence the lowest possible temperature for the oxidation reaction of chloral hydrate to trichloroacetic acid would be the one just above the melting point of chloral hydrate. Below this temperature, solid chloral hydrate would separate from the liquid phase. If the reaction is carried out in the liquid phase, all the undesirable reactions are eliminated; the heat evolved during the reaction can also be easily dissipated so as to control the desired reaction temperature.

OXIDATION OF CHLORAL HYDRATE IN LIQUID PHASE

Oxidation of chloral hydrate can be carried out by means of different oxidizing agents, the choice being restricted to those reacting in acidic medium, as an alkaline medium would lead to the decomposition of chloral hydrate to chloroform. Moreover, only those oxidizing agents stable at 60°C. (an optimum temperature just above the melting point of chloral hydrate) can be used. Nitric acid fulfils all these conditions. It maintains acidic medium throughout and has the advantages of being cheap and readily available. Further, the reaction product obtained is less contaminated and not decomposed by the presence of excess oxidizing agent. Nitric acid is available in 65 per cent (w/w) concentration. The trichloroacetic acid can be easily separated by distillation. The overall reaction is:

$$CCl_3CH(OH)_2 + 2HNO_3 = CCl_3COOH + 2NO_2 + 2H_2O$$

The additional quantity of water (in HNO_3) will help minimize the temperature rise due to the heat of reaction.

Oxidation of chloral hydrate with fuming nitric acid to give trichloroacetic acid in 63 per cent yield has been reported by Vogel[9]. However, Parks and Hollingshead[10] report that oxidation of chloral hydrate by fuming nitric acid is unsuccessful. This work is, therefore, repeated to obtain the exact optimum corditiors of the reaction and relevant data for design calculations.

EXPERIMENTAL PROCEDURE AND RESULTS

Oxidation of chloral hydrate with nitric acid was carried out in an all-glass apparatus at temperatures of 30°, 60° and 70° with suitable stirring. The ratio of chloral hydrate to nitric acid was varied in each case. After the reaction was over the temperature was raised to 110°C. and all the brown fumes of nitrogen dioxide were allowed to escape. The temperature was then raised still further to distil off trichloroacetic acid. Three separate fractions were collected, the fractions and the residue were analysed by standard procedures. The acid content of trichloroacetic acid was determined by titration with standard alkali.

The results (Table 1) show that the reaction is rapid at 60°C. and practically all chloral hydrate is consumed within 6 hr. Overall conversion is 80 per cent; with 10 per cent excess of nitric acid the yield is improved but with 25 per cent excess of nitric acid there is no appreciable difference in the yield. The use of 100 per cent acid is not desirable as it does not offer any advantage. At higher temperatures, side reactions take place and at temperatures below 60°C. the reaction is considerably slow due to the separation of solid chloral hydrate from the liquid phase.

TABLE 1—YIELD OF TRICHLOROACETIC ACID UNDER DIFFERENT CONDITIONS OF OXIDATION

(*Quantity of chloral hydrate, 50 g.; residue, 1·5 g.*)

Nitric acid *ml.*	Molecular ratio $CCl_3CH(OH)_2 : HNO_3$	Temp. °C.	Time *hr*	Yield %
38·6	1 : 2·0	30	192	66·30
38·6	1 : 2·0	30	24	56·70
38·6	1 : 2·0	60	2	63·30
38·6	1 : 2·0	60	4	73·20
38·6	1 : 2·0	60	6	75·70
38·6	1 : 2·0	60	8	76·63
43·0	1 : 2·2	60	6	80·56
48·2	1 : 2·5	60	6	77·85
43·0	1 : 2·2	70	6	74·87
28·0*	1 : 2·2	60	6	79·71
43·0	1 : 2·2	60	4	77·00

* 100%

Based on these results a typical experiment on a slightly larger scale was performed. The data on analysis of the different fractions were made use of for material balance. Thus, a sample of 400 g. of chloral hydrate was oxidized with 344 ml. of nitric acid. The reaction mixture was kept overnight at 30°C. and subsequently heated to 60°C. for 4 hr. The contents were later distilled. The data of this experiment are given below:

Input		Output	
Chloral hydrate	400 g.	Gases	196 g.
Nitric acid	479 g.	Fraction I	161 g.
		Fraction II	251 g.
		Fraction III	264 g.
		Residue	7 g.
Total	879 g.		879 g.

The yield is 71 per cent. The analysis of the three separate fractions is given in Table 2.

TABLE 2—ANALYSIS OF FRACTIONS

	Fraction I	Fraction II	Fraction III
HCl, %	0·24	0·7	0·0
HNO_3, %	22·20	45·4	0·0
CCl_3COOH, %	6·35	13·0	99·3
H_2O, %	71·21	40·9	0·7
Total	100·00	100·0	100·0

Calculations for the Design of Reactor

Based on these results and on the analyses of exit gases, design calculations have been made for a reactor producing 250 kg. of trichloroacetic acid.

Since the reaction time is only 4–6 hr, two reactors used alternately, can produce 500 kg. of trichloroacetic acid per day. Hence the reactor is designed for an output of 250 kg.

Material Balance. A typical material balance for an output of 500 kg. of trichloroacetic acid is given below:

Input		Output	
Chloral hydrate	764 kg.	Gases	372·62 kg.
Nitric acid	914 kg.	Fraction I	308·00 kg.
		Fraction II	480·00 kg.
		Fraction III	504·00 kg.
		Residue	13·38 kg.
Total	1678 kg.		1678·00 kg.

Quantity of water required to absorb NO_2=55·5 kg.*
Quantity of dolomite required to neutralize HNO_3 and other fractions=300·0 kg.*

The reactor consists of a glass-lined jacketed vessel with stirring arrangement and fitted with a water condenser which can be used either for reflux or for distillation at atmospheric or sub-atmospheric pressures. The jacket water for reactor as well as the coolant water for the condenser are required to be at 60°C. to maintain chloral hydrate and trichloroacetic acid in

* On the basis of 250 kg. output of trichloroacetic acid

liquid state. If the reactants are mixed and kept overnight, the time of reaction is reduced from 6 hr to 4 hr. Hence, two batches per day are possible by using two reactors of 250 kg. with a common absorber assembly. The dimensions of the assembly are given below:

Reactor. Basis: 250 kg. of CCl_3COOH

Total volume of reaction mixture	= 577 litres
Diameter of vtessel	= 0·914 m. (assumption)
Height of jacke	= 0·9 m.
Volume of dished head	= 52 litres
Total volume (volume of mixture with 50% excess)	= 870 litres
Volume of cylinder (870—52)	= 818 litres
Height of the cylinder	= 1·24 m.
Thickness of the cylinder	= 1·02 cm.
Annular space of the jacket	= 2·54 cm. (assumption)
Thickness of external shell	= 0·6 cm.
Power requirement for stirring	= 0·5 h.p. motor

Condenser. The quantity of heat to be removed is 48,600 k. cal./hr. Assuming the overall heat transfer coefficient to be 366 C.G.S. units and the temperature of inlet water to be 60°C., the area of the condenser works out to 1·67 sq. m.

Absorber. Assuming the absorption to take place in 4 hr, the diameter of the absorber works out to 0·25 m. and the height, 2·44 m. The exit gases from the absorber and their weights and the effluents from the absorber and dolomite bed and their weights are given in Table 3.

TABLE 3—WEIGHTS OF EXIT GASES FROM ABSORBER AND OF EFFLUENTS FROM ABSORBER AND DOLOMITE BED

	Weight of gas/effluent, *kg.*	
	Absorber	Dolomite bed
O_2	0·96	—
N_2	118·50	—
CO_2	69·35	—
$Ca(NO_3)_2$	29·4	187
$Mg(NO_3)_2$	26·5	165
$(CCl_3CO_2)_2Ca$	—	46
$(CCl_3CO_2)_2Mg$	—	44

Acknowledgement

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Concentration of Rectified Spirit using Solid Desiccants

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Experiments have been conducted using fixed and fluidized beds on dehydration of rectified spirit by anhydrous calcium sulphate at different particle sizes, temperatures, contact times and flow rates of alcohol. The results have shown that 99 0 per cent alcohol can be prepared from rectified spirit and that fixed bed is better than fluidized bed for enrichment. A theoretical analysis of the dehydration mechanism has also been made.

Absolute alcohol is produced from rectified spirit mainly by azeotropic distillation, although in certain cases extractive distillation is preferred. Azeotropic distillation in which benzene is used as entrainer is a fairly old method and is commercially successful also. Nevertheless, steam consumption in these methods has been found to be more than the thermodynamic minimum. It is generally accepted that the actual steam consumption is about 8·5 lb./gal., though the value varies from country to country. Ibrahim *et al.*[1] have shown that the thermodynamic minimum requirement of steam for the production of one gallon of absolute alcohol from rectified spirit is only 4·2 lb.

A survey of literature indicates that only azeotropic distillation has been studied thoroughly. Other methods, viz. extractive distillation and concentration using solid desiccants, have received little attention. Wentworth *et al.*[2] made an attempt to achieve steam economy by using ethyl ether as entrainer instead of benzene. Although considerable economy is claimed by this method, it has not been commercially successful as it involves the use of high pressures. Wallis[3] has reported a solid desiccant method as early as 1936. During World War II the Germans are reported to have used this method on a large scale. But no fundamental study seems to have been carried out so far on this process. Hence this method was chosen by the authors for a detailed study. The aim of the study, in general, was to find out whether steam consumption for the concentration of rectified spirit to absolute alcohol could be brought nearer the thermodynamic value and in particular, to assess the mechanism of the driving force. The results of the study leading to the understanding the mechanism of the driving force are reported in this paper.

EXPERIMENTAL PROCEDURE AND RESULTS

The apparatus consisted of a stainless steel reactor with a diameter of 5 cm. and height of 75 cm., a stainless steel preheater, condenser, assembly and suitable instruments to measure temperature and flow rates. Rectified spirit preheated to the reaction temperature was passed over the desiccant powder in the reactor. The vapours coming out of the reactor were condensed and analysed immediately. When the activity of the desiccant decreased, it was regenerated in the reactor itself.

The effect of the following parameters on the dehydration of rectified spirit has been studied: (i) particle size of the desiccant, (ii) temperature, and (iii) contact time. The particle size was varied from $-28+40$ to $-100+150$ mesh and the temperature of the reactor, from 80° to 150°C. and contact time from 6 to 25 sec. Experiments were conducted both in the fixed bed and fluidized bed conditions at different flow rates using anhydrous calcium sulphate, calcined aluminium sulphate, anhydrous magnesium sulphate, potassium sulphate and dehydrated alum as desiccants. The data obtained with anhydrous calcium sulphate were used to assess the mechanism of the driving force of the concentration process and to find the effect of the modified Reynold's number on mass transfer factor. The effect of temperature at different space velocities of rectified spirit in the case of anhydrous calcium sulphate is shown in Table 1. The effect of modified Reynold's number on mass transfer factor is shown in Table 2.

TABLE 1—EFFECT OF TEMPERATURE ON ENRICHMENT OF RECTIFIED SPIRIT

(Weight of anhydrous calcium sulphate, 25 g.; height of bed, 12·5 cm.; particle size, $-28+40$ mesh; initial conc. of alcohol, 93·5% by volume; duration, 45 min.)

Rate of alcohol g./hr	Temp. °C.	Final conc. by volume %	Enrichment %	Remarks
65·0	80·0	93·5	0·0	Fixed bed
65·0	90·0	96·1	2·6	Fixed bed
65·0	100·0	97·5	4·0	Fixed bed
65·0	110·0	98·1	4·6	Fixed bed
65·0	120·0	99·0	5·5	Fixed bed
65·0	130·0	94·3	0·8	Fixed bed
65·0	140·0	94·0	0·5	Fixed bed
65·0	150·0	93·5	0·0	Fixed bed
195·0	120·0	96·0	2·5	Fluidized bed

TABLE 2—EFFECT OF MODIFIED REYNOLD'S NUMBER ON MASS TRANSFER FACTOR

(*Temperature*, 120°C.)

Rate of alcohol *g./hr*	Contact time *sec.*	Final conc. by volume %	Enrichment %	$N'_{Re} \times 10^4$	j	Remarks
50	26·4	99·0	5·5	1·24	5·5	Fixed bed
65	20·3	99·0	5·5	1·61	4·5	Fixed bed
90	14·6	98·5	5·0	2·22	5·5	Fixed bed
100	13·2	98·0	4·5	2·48	5·7	Fixed bed
130	10·1	97.5	4·0	3·22	5·5	Fixed bed
150	8·8	96·0	2·5	3·70	6·0	Fluidized bed
195	6·7	96·0	2·5	4·83	5·8	Fluidized bed
210	6·3	96·0	2·5	5·20	5·8	Fluidized bed

From the data shown in the tables, it is clear that the azeotrope is broken and it is possible to get 99 per cent alcohol from 93·5 per cent alcohol. The optimum temperature is found to be 120°C. and the optimum range of contact time is 15–25 sec. and the particle size range is $-28+40$ mesh. The data in respect of particle size have not led to any conclusive results, and hence further work is needed on this parameter.

THEORETICAL ANALYSIS AND DISCUSSION

Jury and Licht[4] as a result of study of adsorption of water vapour on anhydrous calcium sulphate have observed that there are steady state and unsteady state regions in the process of adsorption. At very low flow rates and with particle size range greater than 20–40 mesh, the duration for steady state is fairly long. If the percentage enrichment of alcohol is plotted against the time of run for each desiccant the enrichment is found to fall beyond a characteristic time for each desiccant. This time is known as break time. This break time helps us to know whether the process is in steady state or in unsteady state. When the break time is plotted against the average granule diameter the duration of steady state for the particular size can be assessed. In the present work the experiments were restricted to steady state conditions only by taking the particle size range from $-28+40$ mesh to $-60+90$ mesh and conducting the experiments at N'_{Re} less than 10^{-4} and keeping the duration of experiments from 30 to 45 min. which is less than the break time. If the duration of experiments goes beyond the break time value unsteady state sets in. Under these conditions, the mathe-

matical development given below represents only the steady state conditions.

Anhydrous calcium sulphate does not chemically react with alcohol in this process and so alcohol can be considered as an inert gas carrying water vapour along with it. The water vapour is adsorbed on the surface of calcium sulphate. The mechanism of transfer of water from the rectified spirit to the surface of the desiccant can be assumed to consist of the following operations: (i) transfer of water molecules through the gas film around calcium sulphate particles, (ii) transfer of water molecules from the external surface of calcium sulphate through the mouth of the pores to the interior of pores by molecular and Knudson diffusion, and (iii) adsorption of water molecules on the pore wall of calcium sulphate.

Mass transfer through gas film around calcium sulphate particles under (i) is represented by

$$\frac{1}{m}\frac{dN}{d\theta} = k'_f(P_f - P_p).$$

Diffusion of water inside calcium sulphate particles under (ii) is represented by

$$\frac{1}{m}\frac{dN}{d\theta} = k'_D(P_p - P_i).$$

Rate of adsorption of water by activated calcium sulphate as given in (iii) can be represented by

$$\frac{1}{m}\frac{dN}{d\theta} = k'_R(P_i - P^*).$$

Now the relationship between the overall mass transfer coefficient and individual resistances can be written as

$$K\triangle P = \frac{(P_f - P_p)_m + (P_p - P_i)_m + (P_i - P^*)_m}{\frac{1}{k'_f} + \frac{1}{k'_D} + \frac{1}{k'_R}}.$$

A material balance in the reactor for water gives

$$\frac{dN}{d\theta} = \frac{W}{\pi}(P_1 - P_2). \qquad (1)$$

Summing up, the general mass transfer equation can be expressed as

$$\frac{dN}{d\theta} = Km\triangle P. \qquad (2)$$

Comparing Equations (1) and (2)

$$K = \frac{dN}{d\theta}\cdot\frac{1}{m\triangle P} = \frac{W(P_1 - P_2)}{m\pi\triangle P}. \qquad (3)$$

This final equation necessitates the knowledge of K for evaluating $\frac{dN}{d\theta}$. Knowing this value and applying Equation (3) to experimental results the number of moles of water transferred in time θ can be calculated. The

above equation can be easily converted into conventional area units when appropriate effective surface area for mass transfer per unit mass of anhydrous calcium sulphate $\left(\frac{dN}{dA}\right)$ is known.

$$\frac{dN}{dA} = K \triangle P_m \tag{4}$$

$$\text{or } dN = \frac{(P_2 - P_1)\, GS}{\pi\, M_m} = K \triangle P_m\, A \tag{4a}$$

Chilton and Colburn[5] rearranged the terms of Equation (4a) and developed an expression involving the ratio change in particle pressure to the mean particle pressure difference between the gas mixture and the surface, which is

$$j = \left(\frac{P_1 - P_2}{\triangle P_m}\right)\left(\frac{S}{A}\right)\left(\frac{\mu}{\rho D}\right)^{\frac{2}{3}}$$

$$= \frac{K}{G/M_m}\ (\mu/\rho D)^{\frac{2}{3}}$$

$$= \frac{K\, M_{av.}\, P}{\theta}\ (N_{Sc})^{0.66}. \tag{5}$$

Once again for evaluating j a knowledge of K is necessary. However, for the actual experimental data K can be calculated for various rates of G from Equation (5).

Many workers including Gamson[6], Chu[7], Hsu[8] and Leva[9] have correlated j as a function of N'_{Re} of the form, $j = a\,(N'_{Re})^{b}$. But all their experiments were conducted at fairly high N'_{Re}. In these studies, j was found to be a function of N'_{Re}. The present work deals with the Reynold's number range from 10^{-2} to 10^{-4} which has not been explored previously. A critical analysis of the data obtained so far shows that j is fairly constant for all the rates of G. It is quite probable that the variation of j can be considered as a constant for the low N'_{Re} studied in this work. This has also been indicated by Chilton and Colburn[5]. The enrichment has been found to be better if the experiments were conducted in fixed bed conditions. This can explain the diffusion mechanism assumed in developing the theoretical analysis. McCune and Wilhelm[10] and Chu[7] have found that at a given velocity of N'_{Re} a fixed bed is a more effective instrument in mass transfer than the same bed in fluidized bed conditions.

Nomenclature

K = Overall mass transfer coefficient, lb. moles / (hr) (sq. ft) (atm.)

P = Overall mean partial pressure driving force, mm. of Hg

P_f = Average partial pressure of water in gas stream, mm. of Hg

P_1 = Partial pressure of water at pore wall, mm. of Hg

P_p = Partial pressure of water at external surface of $CaSO_4$ particles, mm. of Hg

P^* = Equilibrium partial pressure based on adsorbate content of $CaSO_4$, mm. of Hg

k'_f = Gas film mass transfer coefficient, $\frac{\text{gram moles}}{(\text{sec.})(\text{g.of } CaSO_4)(\text{mm. of Hg})}$

K'_R = Rate coefficient of adsorption, $\frac{\text{gram moles}}{(\text{sec.})\ (\text{sq. cm.})\ (\text{mm. of Hg})}$

K'_D = Diffusion mass transfer coefficient inside solid, $\frac{\text{gram moles}}{(\text{sec.})(\text{g.of } CaSO_4)(\text{mm. of Hg})}$

m = Weight of $CaSO_4$, g.

N = Water transferred, gram moles

θ = Time, sec.

π = Total pressure, atm.

P_1 = Partial pressure of water in entering gas stream, mm. of Hg

P_2 = Partial pressure of water in exit gas stream, mm. of Hg

W = Gas rate, gram moles/sec.

G = Mass velocity, lb./(hr) (sq. ft)

S = Cross-sectional area, sq. ft

A = Surface area, sq. ft

M_m = Mean molecular weight

N_{Sc} = $\mu/\rho D$=Schmidt number.

N'_{Re} = Modified Reynold's number

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Development of HMX for Utilization in Powerful Explosives

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Cyclotetramethylenetetranitramine (HMX or high melting explosive) is an important substance in the preparation of powerful explosives. A mixture of HMX (β-polymorph), RDX (cyclotrimethylenetrinitramine), TNT and beeswax has a greater detonation velocity than a mixture of RDX and TNT (60:40).

The reaction mechanism for the formation of HMX by using Bachmann reagents has been described. The preparation of HMX by direct action of hexamine, nitric acid (98%), ammonium nitrate and acetic anhydride as well as through 1, 5-methylene-3, 7-dinitro-1, 3, 5, 7-tetrazacyclooctane has been described. The effect of crystal structure of HMX on the density and sensitivity has also been discussed.

HMX, a high melting explosive—chemically designated as cyclotetramethylenetetranitramine or octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine or 1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazacyclooctane—has been reported as a by-product formed along with RDX (cyclotrimethylenetrinitramine) in the nitrolysis of hexamine by Hale's[1], Ross-Schiessler and Bachmann combination[2] processes. This was confirmed during an inspection of one of the war-time plants which manufactured cyclonite by Hale's process. A scaly deposit on the apron of a classifier filter had formed when the diluted reaction mixture was cooled and this was found to be almost pure HMX[3]. Its structure as 1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazacyclooctane was suggested by Bachmann in 1941 and subsequently confirmed by Wright and coworkers[4,5] in 1949. Recently, Ray Pepinsky[6] has studied the structure of HMX by X-rays and neutrons. Cachia and Whitbread[7] have described a gap-test for the sensitivity to shock of this explosive along with RDX, TNT and PETN.

In view of the greater sensitivity of HMX compared to RDX, it is not suitable as a service explosive. Hence, the possibility of developing from HMX powerful high explosives by incorporating small quantities of other explosives like RDX, TNT, etc. and a suitable phlegmatizing wax was studied. Of the four polymorphic forms, α, β, γ and δ, in which HMX exists, the first two are of common occurrence. All the four forms can be distinguished by microscopic examination, infrared spectra and Rotter sensitiveness tests. The α-polymorph is very sensitive to impact and can be

utilized in combination with other explosives as an initiator or explodering charge. β-HMX is the most stable form and may be utilized as an important constituent of the main fillings of the shells and in warheads of the guided weapons.

The advantage of using HMX is that its stable form, β-HMX has approximately 5 per cent more density than that of RDX (β-HMX, 1·91 g./cc.; RDX, 1·81 g./cc.). Though HMX and RDX have the same elementary composition and the available energy per gram of the two compounds is almost identical, yet the use of higher density compound (HMX) in explosive compositions increases their densities and hence results in higher velocity of detonation and greater explosive power. In explosive mixtures containing HMX, it is possible to attain a detonation velocity greater than 7700 m./sec. which is that of RDX/TNT mixture (60 : 40), while maintaining the figure of insensitiveness nearly the same. This higher velocity of detonation may improve the hollow charge effect both in penetrating power and cavity volume. It also leads to an increase in the lethality of a fragmenting charge.

A simple procedure for making HMX in good yield starting from raw materials like hexamine, nitric acid, acetic anhydride and ammonium nitrate is not available so far. Wright and coworkers[5,8] and Bachmann and others[9] had obtained HMX (in 28 per cent yield based on hexamine) through 1, 5-methylene-3, 7-dinitro-1, 3, 5, 7-tetrazacyclooctane (DPT) starting from hexamine. Fisher[10] has also mentioned its formation utilizing the above reagents. The reactions for producing RDX and HMX are closely related and the reagents employed are also the same. The three procedures by which RDX is manufactured are given below:

1. Hale's process[1] (Nitrolysis)

$$C_6H_{12}N_4 + 4HNO_3 \rightarrow (CH_2N_2O_2)_3 + NH_4NO_3 + 3CH_2O$$

The yield of RDX is 80 per cent on the basis of hexamine. RDX is contaminated with HMX.

2. Ross-Schiessler process[11]

$$3CH_2O + 3NH_4NO_3 + 6Ac_2O \xrightarrow{70°} (CH_2N_2O_2)_3 + 12AcOH$$

RDX is obtained in 60 per cent yield based on formaldehyde; it is contaminated with HMX.

This method involves as its first step the synthesis of hexamethylenetetramine.

$$6CH_2O + 4NH_4NO_3 + 3Ac_2O \rightarrow C_6H_{12}N_4 + 4HNO_3 + 6AcOH$$

and as the second step a Hale nitrolysis,

$$C_6H_{12}N_4 + 4HNO_3 \rightarrow (CH_2N_2O_2)_3 + NH_4NO_3 + 3CH_2O$$

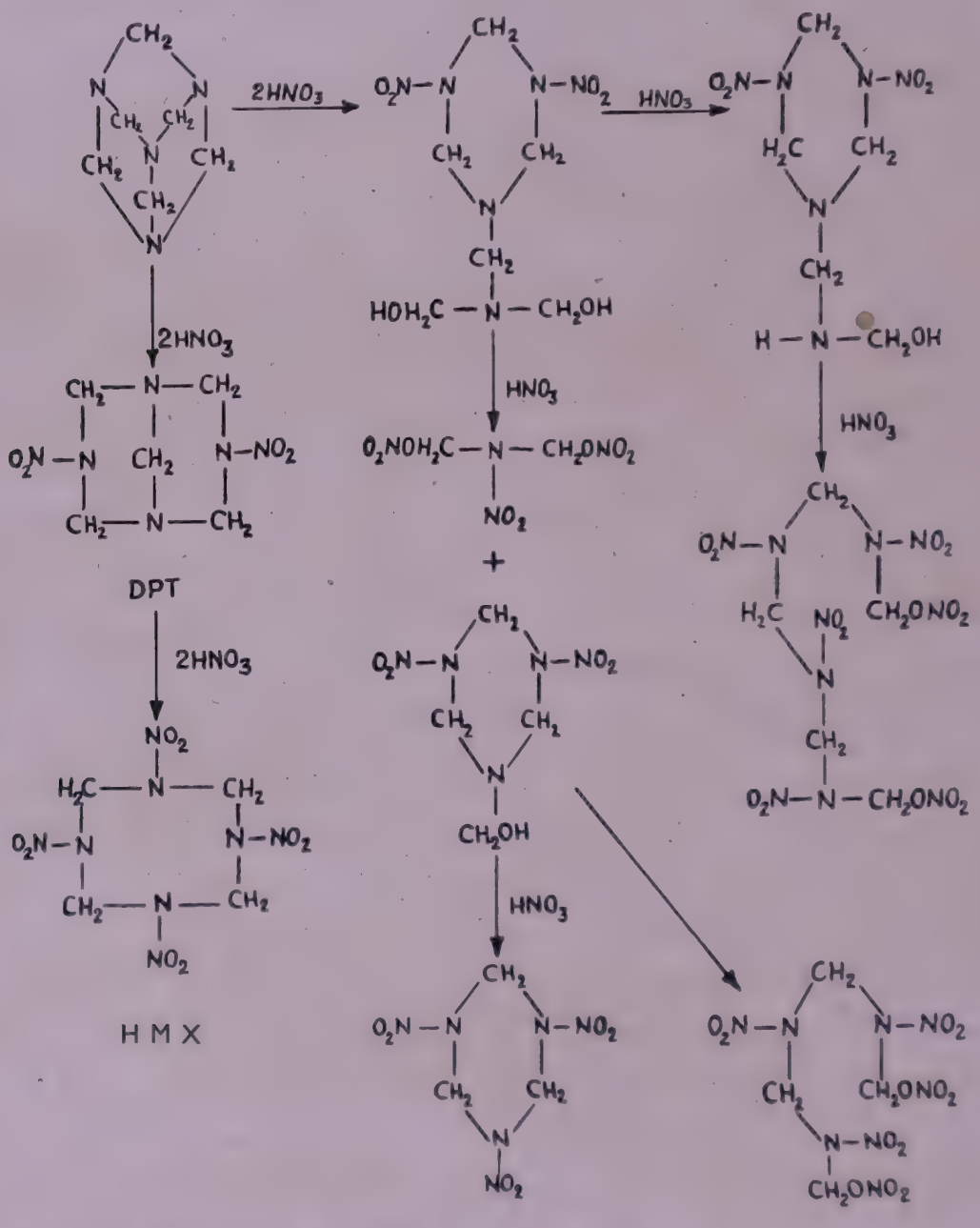
In the third step the non-explosive products of the second step together with more ammonium nitrate and acetic anhydride, undergo the first reaction.

3. Bachmann combination process[2]

$$C_6H_{12}N_4 + 2NH_4NO_3 + 4HNO_3 + 6Ac_2O \xrightarrow{65\text{-}75°} 2(CH_2N_2O_2)_3 + 12AcOH$$

The yield of RDX is 80 per cent on the basis of formaldehyde. The compound contains about 5 per cent HMX. Besides, 1, 7-diacetoxy-2, 4, 6-trinitro-2, 4, 6-triazaheptane (BSX); 1, 9-diacetoxy-2, 4, 6, 8-tetranitro-2, 4, 6, 8-tetrazanonane (AcAn) and other products are formed.

In Hale's process the formation of different products could be explained from the following scheme:

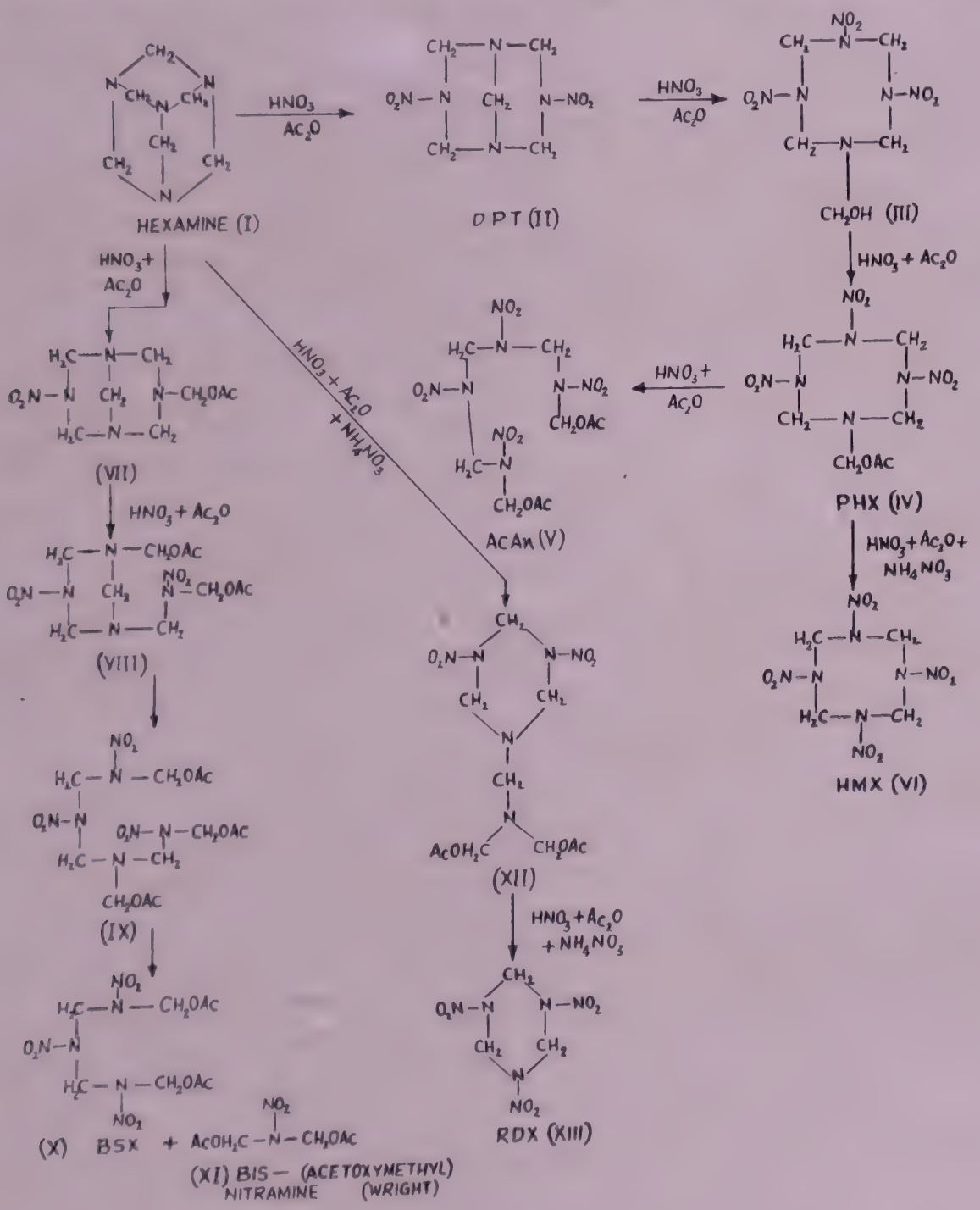


For the preparation of HMX the same reagents as are used in Bachmann combination process are employed and the reaction can be written as:

$$2C_6H_{12}N_4 + 4NH_4NO_3 + 8HNO_3 + 12Ac_2O \xrightarrow{45\text{-}50^\circ} 3(CH_2N_2O_2)_4 + 24AcOH$$

In the case of RDX the reaction conditions are so chosen as to get

high acidity and high activity of the nitrating agent particularly in the initial attack on the hexamine molecule. During the preparation of HMX the conditions are so adjusted as to get low acidity and low activity of the nitrating agent. In the preparation of RDX, acetic anhydride is taken in the flask and to it two solutions of hexamine in acetic acid, and ammonium nitrate in 98 per cent nitric acid are simultaneously added at 65–75°C. On the other hand, during the preparation of HMX, the solution of hexamine in acetic acid is taken in the flask, acetic anhydride and the solution of ammonium nitrate in 98 per cent nitric acid are poured with a lead of the ammonium nitrate solution (temperature, 45–50°C.). It has been observed



that hexamine undergoes two different types of cleavage giving: (i) compounds with four amino-nitrogen atoms as DPT, HMX and the linear tetranitramine (AcAn), and (ii) compounds having three amino-nitrogen atoms as RDX and the linear trinitramine (BSX). The first type of cleavage occurs when there is lower acidity and low activity of the nitrating agent than in the formation of class (ii) compounds.

The reaction mechanism for the formation of HMX and its allied products may be given as:

Hexamethylenetetramine (I) first reacts with nitric acid to give 1, 5-methylene-3, 7-dinitro-1, 3, 5, 7-tetrazacyclooctane, DPT (II). This, when treated with 98 per cent nitric acid in the presence of acetic anhydride, produces 1-acetoxymethyl-3, 5, 7-trinitro-1, 3, 5, 7-tetrazacyclooctane, PHX (IV) due to the cleavage of the endomethylene bridge in DPT (II). This reaction proceeds through the hydroxy compound (III). PHX (IV) on treatment with nitric acid and acetic anhydride undergoes scission in the ring and yields 1, 9-diacetoxy-2, 4, 6, 8-tetranitro-2, 4, 6, 8-tetrazanonane AcAn (V), a linear product. On the other hand, when ammonium nitrate is added to the reaction mixture the eight-membered ring is left intact and there is replacement of acetoxymethyl group by a nitro group yielding HMX (VI). The formation of RDX (XIII) along with HMX (VI) could be either due to the ring closure of the linear trinitramine, BSX (X) formed as a by-product during the reaction or by a Ross-Schiessler synthesis from the formaldehyde liberated from the acetoxymethyl group in PHX (IV). In the above reactions it is observed that there is introduction of a single nitro group at a time. The bridge is ruptured first and then the eight-membered ring.

Similarly the formation of BSX (X) when hexamine (I) is treated with nitric acid and acetic anhydride can be explained through (VII), (VIII) and (IX), considering that rupture would take place away from the nitramine group and close to the nitrogen carrying an acetoxymethyl group. In the presence of ammonium nitrate the formation of RDX (XIII) could also be explained through (XII).

In the preparation of HMX (VI) from hexamine (I) it is almost certain that the reaction proceeds through DPT (II) and PHX (IV).

The important factors that contribute towards good yield of HMX during its preparation from hexamine, ammonium nitrate, 98 per cent nitric acid, acetic anhydride and acetic acid are: (i) the molar ratios of the various reactants, (ii) the dilution of the reaction mixture with acetic acid, (iii) the rate of additions of the ammonium nitrate-nitric acid solution and acetic anhydride to hexamine-acetic acid solution, and (iv) the temperature.

It should be possible to get higher yields of HMX by the combination process than through DPT and PHX for which conditions are being standardized.

The crude HMX obtained after simmering contains about 33 per cent RDX which is separated by repeated crystallizations from acetone. HMX required for explosive compositions should not contain more than 0·2 per cent RDX, otherwise this impurity hinders in its inspection.

The polymorphic form of HMX obtained depends upon the solvents and the conditions of crystallizations. Thus, α-HMX could be obtained in hairy needles by crystallizations from 70 per cent hot nitric acid, ethyl alcohol, and immediate crystallization from glacial acetic acid. The β-polymorph was obtained by slow crystallization from excess of solvents, for example, acetone, glacial acetic acid, and mesityl oxide. On scratching the sides of the flask containing the solution of the explosive in glacial acetic acid a mixture of the polymorphs was obtained. The γ-HMX was obtained in triangular plates by precipitating it from the acetone solution of HMX with water. The conversion of β-HMX to δ-HMX could be effected by heating the former on a hot stage microscope at 240–50°C. and was complete at 270°C. Crystallization of HMX from isovaleric acid at 160–170°C. also gave δ-HMX as cigar-shaped crystals.

Photomicrographs of the various forms are shown in Fig. 1. The crystal densities and the impact sensitivities of some of the samples are recorded in Table 1.

Amongst the four polymorphs, β-HMX is the most stable, whereas δ-HMX is metastable even at room temperature.

In common practice β-HMX is generally associated with the more sensitive form, α-HMX. The addition of a few α-HMX crystals to the β-form increases the sensitivity of the latter. Therefore, extreme precautions are required to get the β-crystals completely free from α-crystals. Specifications for β-HMX to be employed in making powerful explosive compositions require that there should not be any α-count in two thousand β-counts.

TABLE 1—CRYSTAL DENSITIES AND IMPACT SENSITIVITIES OF SOME POLYMORPHS OF HMX

Solvent & conditions of crystallization	Crystalline form	Crystal density *g./cc.*	Impact sensitivity* (mean height for 50% explosions) *cm.*
Conc. nitric acid	α	1·88	6
Acetone	β	1·91	20
Acetone solution precipitated with water	γ	1·82	21
Isovaleric acid at 160–70°C.	δ	1·76	5

* Impact sensitivities of α, γ and δ polymorphs depend upon the thickness of the crystals.

All the four polymorphs have characteristic infrared spectra, and could be easily distinguished (Fig. 2). The spectra were taken with Nujol (Perkin Elmer 221 model) using sodiumc hloride prism. The interpreta-

FIG. 1—PHOTOMICROGRAPHS OF DIFFERENT POLYMORPHIC FORMS OF HMX

[*a*, FROM ETHYL ALCOHOL AFTER 12 HR (α-HMX); *b*, FROM ETHYL ALCOHOL AFTER 3-4 DAYS (α-HMX); *c*, FROM CONC. NITRIC ACID (α-HMX); *d*, FROM ACETONE (β-HMX); *e*, FROM MESITYL OXIDE (β-HMX); *f*, FROM GLACIAL ACETIC ACID—IMMEDIATE CRYSTALLIZATION ON COOLING (α-HMX); *g*, FROM GLACIAL ACETIC ACID AFTER SCRATCHING (MIXTURE); *h*, FROM EXCESS GLACIAL ACETIC ACID AFTER 5-6 DAYS (β-HMX); *i*, FROM ACETONE + WATER (γ-HMX); *j*, β-HMX HEATED AT 240-50 C. ON HOT STAGE MICROSCOPE—CONVERSION TO δH.M.X; *k*, β-HMX HEATED AT 260-70 C. ON HOT STAGE MICROSCOPE—COMPLETE CONVERSION TO δ-HMX]

tion for the difference in infrared spectra of the polymorphs on the basis of X-ray diffraction and Raman spectra will be the subject of a separate communication.

EXPERIMENTAL PROCEDURE

HMX from Hexamethylenetetramine. Hexamethylenetetramine (420 g.) was dissolved in a minimum quantity of glacial acetic acid (650 ml.) and the solution taken in a 5-litre, three-necked flask. A solution of ammonium nitrate (450 g.) in 98 per cent nitric acid (500 ml.) was prepared with proper cooling so that the temperature did not rise above 25°C.; this was taken in a separating funnel. In the second separating funnel acetic anhydride (1701 ml.) was taken. Hexamine solution was well stirred and its temperature was raised to 50°C. on water bath. The contents of the separating funnels were gradually added with a lead of ammonium nitrate solution, and the contents of the flask were kept well cooled with ice-sodium chloride mixture. The reaction is highly exothermic and hence extreme precautions are required in controlling the additions of the reactants and the temperature. The duration of the additions was 2 hr, after which the reaction mixture was further stirred at the same temperature for 1 hr. During addition, crystallization and dissolution of the intermediate products take place twice, and finally HMX with RDX, BSX, AcAn, etc. crystallizes out.

The slurry was mixed with distilled water (4·9 litres) in order to bring the acetic acid concentration to 33 per cent. The product was well simmered for 4 hr on boiling water bath, when there was profuse evolution of formaldehyde. It was cooled, filtered, well washed with hot water on a Buchner, and dried (crude product, 475 g.). This was crystallized five times from excess of acetone. HMX which is less soluble than RDX in this solvent came out as a mixture of α- and β-polymorphs due to rapid crystallization; yield, 290 g. (21·7 per cent based on hexamine), m.p. 281·5°C.

DPT (1, 5-Methylene-3, 7-dinitro-1, 3, 5, 7-tetrazacyclooctane). Two solutions were prepared. The first solution was prepared by dissolving 100·8 g. of hexamine in 160 ml. of glacial acetic acid. The second was prepared by adding gradually 63 ml. of nitric acid (98 per cent) to 180 ml. of acetic anhydride which was kept stirred; the temperature was kept below 15°C. during addition and the solution was immediately used. These two solutions were added gradually to 30 ml. of acetic acid, which was kept stirred. The reaction temperature was maintained at 25–30°C. throughout the addition period (1 hr). The mixture was stirred for another half an hour at the same temperature. When water (400 ml.) heated to 65°C. was added to the mixture DPT was precipitated; this was filtered and washed with water; yield, 75 g. (48·7%), m.p. 198°C. (decomp.). The crude product was used as such.

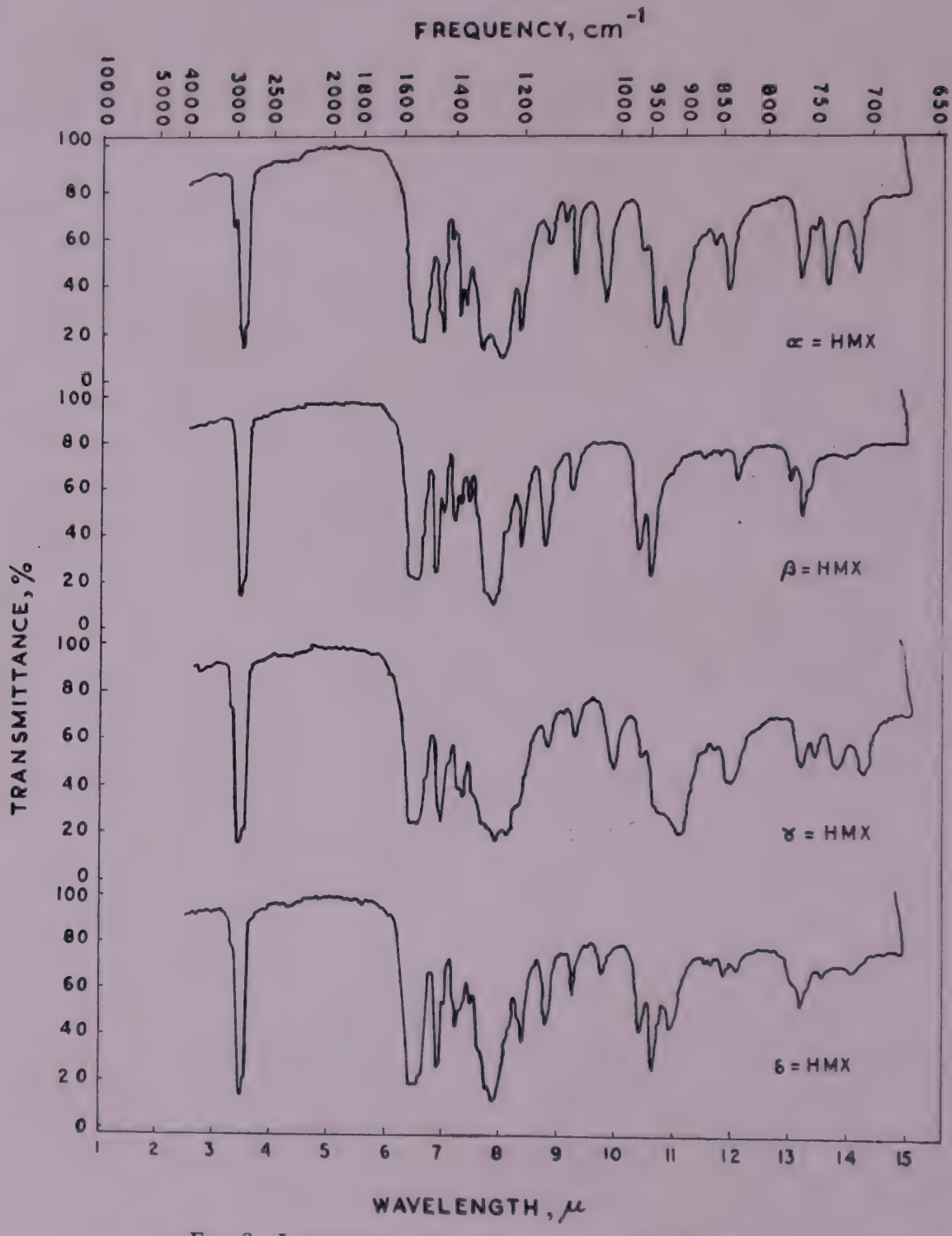


FIG. 2—INFRARED SPECTRA OF POLYMORPHS OF HMX

HMX from DPT. A suspension of DPT (50 g.) in acetic anhydride (230 ml.) was taken in a three-necked flask and the temperature raised to 60°C. on a water bath. A solution of ammonium nitrate (22 g.) in 98 per cent nitric acid (23·5 ml.) was prepared (temperature, below 25°C.) and allowed to stand till there was no more evolution of nitric oxide fumes. This solution was carefully added during a period of 1 hr, maintaining the same temperature throughout the reaction. The reaction was highly exother-

mic in the beginning. After the later half of the addition period HMX started crystallizing out. After the addition was complete the mixture was stirred for 1 hr at the above temperature and cooled to 50°C. Water (225 ml.) was then rapidly added to the mixture which was simmered on a steam bath for 12 hr, cooled, filtered; the crystals were washed with hot water. The product was crystallized from acetone, m.p. 280°C.; yield, 38 g. (55% based on DPT).

PHX (**1-acetoxymethyl-3, 5, 7-trinitro-1, 3, 5, 7-tetrazacyclo-octane**). A suspension of 10 g. of DPT in 46 ml. of acetic anhydride was taken. To this 2 ml. of 98 per cent nitric acid (sp. gr., 1·52) were rapidly added, while keeping the mixture well stirred. The reaction was exothermic. DPT went into solution, slowly after which PHX started crystallizing out as white needles. The crystals were filtered, washed with acetone, and dried, (yield, 11·7 g.)

HMX from PHX. A mixture of glacial acetic acid (60 ml.), acetic anhydride (10 ml.) and ammonium nitrate (10 g.) was taken in a three-feeder flask and the reaction mixture was maintained at 65°C. throughout the reaction. Acetic anhydride (20 ml.), PHX (17 g.) and a solution of ammonium nitrate (7 g.) in 98 per cent nitric acid (6 ml.) were added to the stirred mixture during a period of 15 min. After another 20 min. water (200 ml.) was added and the crystalline mass filtered, washed with water and collected (14·5 g.). This was simmered with 50 per cent acetic acid (200 ml.) containing 1 per cent nitric acid on a steam bath for 5 hr, cooled, filtered, washed with water; crude product, 10 g. This on crystallization from acetone gave pure HMX, m.p. 281°C.; yield, 8·5 g.

Impact Sensitivities. These tests were carried out on different samples by Fall Hammer method using 1 kg. weight. The mean height for 50 per cent explosions was taken.

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Design Considerations for a Reactor for Chemical Exchange Method of Producing Heavy Water

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On the basis of data collected with regard to the reaction, H_2O (l) + HD(g) $\rightleftharpoons$ HDO(l) + H_2(g) in liquid phase, on the choice of catalyst, temperature of reaction, etc. and making some assumptions, important steps to be considered for the design of reactor are given. An experimental set-up has also been proposed.

Heavy water is an excellent moderator-coolant for use in atomic reactors and its economic production is a subject of considerable interest. Of the various methods known to have been used for its production, chemical exchange method represented by the reaction, $H_2O(l) + HD(g) \rightleftharpoons HDO(l) + H_2(g)$ in liquid phase, offers distinct advantage on account of its reversibility. Carried out in liquid phase, the method offers additional advantages in that higher values of equilibrium constant are obtainable in comparison with those for gaseous phase reaction, and heat energy is saved due to saving of heat of vapourization. The raw materials used for the reaction being non-corrosive, the method does not require the use of special materials of construction. The object of the present investigation is to study the above reaction and indicate the important steps to be considered for the design of a reactor for the reaction.

Montarnal *et al.*[1] studied the effect of different variables on the rate of the reaction and found that at normal pressures, the rate of diffusion controlled the overall rate of the reaction, whereas at higher pressures, the chemical reaction rate became more important, and the overall rate constant appeared to be independent of the degree of turbulence imparted. However, Hirota *et al.*[2] found that under constant volume conditions, the degree of turbulence imparted did not apparently influence the overall reaction rate till the partial pressure of the gaseous phase was not altered. Becker *et al.*[3] and Roth *et al.*[4] have reported that the overall rate constant using finely divided platinum-charcoal or platinum-chromium sesquioxide catalyst increased with temperature, although their data do not appear to indicate the trend as shown by the Arhenius relation between temperature

and reaction rate. With constant agitation, they found that the rate constant increased with the quantity of catalyst initially, and then, remained constant with increase in the quantity of catalyst.

The reaction has been reported to be of the first order[2,3]. Further, results obtained by the previous workers[1–4] appear to indicate that neither diffusion nor chemical reaction completely controls the reaction, and that overall rate controlling factors appear to be a combination of both the processes, and under certain conditions of operation, either of the two processes might have predominating influence. Irrespective of this fact surface area available between the phases plays a very important part. This basic fact was not realized by any of the previous workers. Although Becker *et al.*[3] found that the reactor volume required by using 0·7 mm. sieve plate as contacting device for gas-liquid system was less than that required by using 1 mm. sieve plate for the purpose, the underlying basic fact appears to have remained unnoticed. The object of the present investigation is, therefore, to bring forth this fundamental aspect and indicate the necessity of dividing the gas stream (in the reaction) into small bubbles in the liquid contained in the reactor so as to increase the surface area in the interphase contact. It is also intended to spotlight the importance of such contacting device in the design of the reactor.

DESIGN CONSIDERATIONS

(i) **Reactor Volume.** The integral form of the rate equation of this first order reaction can be written as:

$$\ln \frac{n_{a_o} - x_o}{n_{a_o} - x} = K\,(t - t_o) \tag{1}$$

$$\ln \frac{C_{E_o}}{C_E} = K\theta \tag{2}$$

where

$n_{a_o} - x_o = C_{E_o}$ = concentration of reactant E in charge to the reactor per unit volume per unit time

$n_{a_o} - x = C_E$ = concentration of reactant E in charge after time interval $(t - t_o) = \theta$

and K = reaction rate constant.

Since concentration $C = \mathcal{N}/V$ and $\theta = V_R/V$,

where $\mathcal{N}$ = number of moles of the component

V = instantaneous volume of the gas stream flowing at any point of the reactor, and

V_R = volume of the reactor

Equation (2) can be written as

$$V_R = V/K \ln \frac{N_{E_o}}{N_E}. \tag{3}$$

In Equation (3), V can be put equal to $(V_1+V_2)/2$, where V_1 and V_2 are the volumes per unit time of the gas flowing in, and out of the reactor, respectively.

In the case of this three-phase heterogeneous (catalytic) reaction, V can be introduced into the reactor either in bulk or dispersed in the liquid phase in the form of small bubbles. In the latter case, increase of surface area of gas-liquid contact is considerable, and such an increase will increase the overall rate of the reaction, thereby, reducing the volume of the reactor for a given conversion. Further, such a distribution of bubbles will help better dispersion of the solid catalyst also in the liquid phase. The increase of surface area ($\triangle S$) due to division of a volume of gas having an average diameter, D, into n smaller bubbles, is easily deducible and can be put in the form:

$$\triangle S = 4\pi(D/2)^2 \ (\sqrt[3]{n}-1). \tag{4}$$

The increase in the overall rate of reaction should be proportional to this increase of surface area. No experimental data, at present, are available, which relate the rate of reaction with various sizes of bubbles in the liquid phase, which also contains the solid catalyst in dispersion. In such a solid-liquid-gas system, in addition to the diffusion and chemical reaction processes, other processes depending on adsorption and desorption might come into play, and make the overall reaction mechanism more complicated. In the absence of any data for such a system, it is desirable to undertake experimental study to find out the quantitative effect of bubble sizes on the rate of reaction in such a complicated system, before such a value can exactly be used in sizing a reactor.

Of the few contacting devices to have the dispersed gas phase in liquid, chain bubbling device, which shoots out a series of bubble streams from closely-made holes (more than, at least, a bubble diameter distance), appears to be quite feasible in such a system, and for which the following relationship[5] can be used:

$$d = \left[\frac{72\rho}{\pi^2 g \triangle\rho}\right]^{1/5} V_g^{0.4} \tag{5}$$

where d = diameter of bubble (mm.)
ρ = density of the liquid phase (g./cc.)
$\triangle\rho$ = difference in density between liquid and gas phases
g = acceleration due to gravity, and
V_g = volumetric flow rate of the gas in the orifice (cc./sec.).

(*ii*) **Height of the Reactor.** For a given conversion, Equation (2) can be used to calculate the required time interval (θ)—a period during which bubbles should be in the reactor. The terminal velocity of bubbles can be calculated from known relationship[5] and by taking into consideration the effects due to nearness of bubbles, their nonspherical nature, etc. and the presence of the dispersed solid catalysts, the height of the reactor can be determined.

From the foregoing representation, it will be seen that although the overall rate of reaction will increase by introducing the gas in the liquid system in the form of small bubbles, with consequent decrease in reactor size, there will be some increase of pressure drop in the system, attended with increase in consumption of energy. Nevertheless, the economy of operation of the process is discernible by striking a balance essentially between the facts, (i) increase of rate of reaction with subdivision of gas into bubbles, and consequent reduction in reactor volume (V_R), and (ii) extra energy required for subdivision of bubbles and the increased pressure drop.

SUGGESTIONS FOR SET-UP

The set-up would, in principle, consist essentially of a tower as contacting device, in which hydrogen gas divided into small bubbles and water flow countercurrently. At the bottom of the reactor, deuterium-rich water is converted into gas in an electrolytic cell, while at the top, the reflux required is provided by converting the hydrogen to water by burning it with oxygen. Since separation factor of the exchange reaction is large (*c.* 3·5-4) at comparatively low temperatures, for example, near the room temperature of 25–30°C., only a few stages will be required to obtain a fair concentration of heavy water.

Acknowledgement

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Studies on Extraction of Uranium, Niobium and Tantalum from Samarskite

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Samarskite contains valuable elements like uranium, niobium and tantalum which are useful in the field of nuclear energy and in steel industry. Bench-scale studies have been carried out on the determination of optimum conditions for the extraction of these metals by different methods, such as alkali fusion, sulphuric acid treatment, ammonium fluoride fusion and chlorination. A solvent extraction process using the system, hexone-hydrofluoric acid-sulphuric acid, has been developed for the extraction, from aqueous solution, of niobium and tantalum and their separation from each other. Niobium and tantalum oxides of more than 99·9 per cent purity have been obtained by this method.

Samarskite, a niobate and tantalate of the general formula AB_2O_6 (where A represents Y, Er, Ce, La, U, Ca, Fe, Pb, Th and B represents Nb, Ta, Ti, Sn or W), occurs with cyrtolite, garnet, muscovite, etc. in pegmatites in some parts of India. The important methods[1] for opening up of niobium and tantalum minerals are: (i) digestion with alkaline or acid solutions, (ii) fusion with alkaline or acid fluxes, and (iii) chlorination. Attempts made in this laboratory to find out a suitable method and to work out the optimum conditions for the recovery of uranium, niobium and tantalum from samarskite, and also to obtain niobium and tantalum in a pure state are given in this paper.

EXPERIMENTAL PROCEDURE

The ore was crushed to -100 $+200$ mesh size. It was found to have the composition: U_3O_8, 10·34; ThO_2, 2·6; rare earth oxides, 15·2; $(Nb \& Ta)_2O_5$, 44·1 (Nb_2O_5, 34·94 & Ta_2O_5, 9·16); TiO_2, 3·9; Fe_2O_3, 10·69; and SiO_2, 2·2 per cent.

Alkali Fusion followed by Acid Leaching. Fusion was carried out in a mild steel crucible at 350–400°C. with different mineral and alkali ratios and with different mesh sizes of the sample for varying intervals of time. The reacted mass was leached with water and then treated with excess hydrofluoric acid. The percentage reaction was calculated assuming that the whole of the rare earths and thorium remained in the residue as fluo-

rides. The soluble portion was precipitated with ammonia and ignited to the oxide. The optimum conditions for opening up of the ore were found to be as follows: mesh size, −100 +200; mineral : alkali :: 1 : 2 (by weight); temperature, 350–400°C.; and time, 1 hr.

It is known that when the fused niobates and tantalates are treated with nitric acid or hydrochloric acid, the impurities are leached out leaving behind enriched concentrates of niobium and tantalum[2]. In the present study sulphuric acid, instead of nitric or hydrochloric acid, was used, as it is cheap and suitable for the subsequent recovery of uranium by the anion exchange method. Five grams of the cake, obtained after alkali treatment and washing with water, were leached with sulphuric acid (100 ml.) of different normalities. The following data were obtained for a leaching period of 4 hr using 10 ml. of sulphuric acid of different concentrations:

Sulphuric acid	Uranium leached out
N	%
0·36	48·2
0·72	84·6
1·08	90·0
1·44	95·4
2·16	98·4

With 1·08*N* sulphuric acid, the *p*H of the final solution adjusted itself to 1·5, which was, incidentally, quite suitable for the recovery of uranium by the ion exchange method. Under this condition the residue settled down after being kept overnight and could easily be filtered. With increase in the concentration of acid the settling rate of the residue became very slow probably due to the formation of colloidal particles, and filtration became difficult.

The rate of dissolution of uranium from the alkali-fused mass was fairly fast and was complete in about an hour's time. The percentage of uranium extracted at different time intervals when 5 g. of the cake were leached with 100 ml. of 1·4*N* sulphuric acid was as follows:

Leaching time	Uranium extracted
hr	%
$\frac{1}{4}$	88
$\frac{1}{2}$	92
$\frac{3}{4}$	94
1	96
$1\frac{1}{2}$	96·5

The residue containing niobium, tantalum, thorium, rare earths, etc. was used for extraction of niobium and tantalum separately. Uranium was separated from iron and other impurities present in the leach solution by anion exchange[3].

Acid Treatment. The alkali fusion method for opening up the mineral followed by acid leaching of the fused cake was quite efficient as far as the extraction of uranium was concerned, and economical from the point of view of cost of chemicals. However, it was thought, that the direct treatment of the ore with sulphuric acid would be advantageous as it would involve lesser number of stages. Hence, sulphuric acid digestion of the ore was studied under different conditions.

The experiments were carried out on 10 g. scale. The mineral was added in small portions to sulphuric acid previously heated to the required temperature. After a known time interval, the reacted mass was cooled and diluted with water. Uranium, iron, etc. went into solution whereas niobium and tantalum remained in the residue due to hydrolysis. The hydrolysed mass, being lighter, could be separated from the unreacted heavier part by careful decantation. The separation by decantation was repeated twice or thrice with extra amounts of water. The optimum conditions for the decomposition of the ore were found to be: mesh size, −100 +200; mineral: sulphuric acid, 1: 2·2 to 2·5; temperature, 200–210°C.; and time, 1 hr. Under these conditions the ore reacted to the extent of 88 per cent. The filtrate contained uranium, thorium and rare earths. An attempt was made to preferentially precipitate thorium and rare earths as oxalates or fluorides from this solution. When thorium and rare earths were precipitated as fluorides, considerable amount of uranium also was precipitated as uranium tetrafluoride, probably due to the presence of ferrous sulphate in solution. To avoid this loss of uranium, ferrous sulphate was oxidized by the addition of about 2 g. of pyrolusite for 100 g. of the ore while heating with sulphuric acid. In this case the loss of uranium during the precipitation of thorium and rare earths as fluorides was negligible.

Ammonium Fluoride Fusion. The ore was fused with ammonium fluoride at 250°C. or with ammonium bifluoride at about 150–180°C. The thin paste obtained after fusion was leached with water. Part of the reacted mass went into solution very easily leaving behind rare earths and thorium fluorides as insoluble fluorides. Part of the uranium also remained in the residue as the quadrivalent fluoride and the remainder went into solution. Uranium could be extracted from the residue by carbonate leaching and precipitated as sodium diuranate by addition of caustic soda. Nickel and graphite crucibles were used in these studies depending on the scale of operation, from 10 g. to 400 g. per batch. While nickel is slightly attacked, graphite is most suitable for the purpose. The optimum conditions were: mesh size, −100 +200; ore : ammonium fluoride : : 1: 3; temperature 200–250°C.; and time, 1-2 hr.

The reaction under these conditions went to about 86 per cent. Niobium, tantalum and uranium present in the solution were precipitated with ammonia and were used for further purification by solvent extraction.

TABLE 1—OPTIMUM CONDITIONS AND METHODS OF TREATMENT OF SAMARSKITE FOR RECOVERY OF U, Ni, & Ta

(Recovery values in per cent of total constituents)

Method	Un-reacted ore	Residue				Filtrate			
		$(Nb, Ta)_2O_5$	R_2O_3	ThO_2	U_3O_8	$(Nb, Ta)_2O_5$	R_2O_3	ThO_2	U_3O_8
Alkali fusion followed by acid leaching*	—	97·7	46·7	73·1	4·4	1·0	51·2	25·0	94·8
Sulphuric acid digestion†	12	77·0	18·4	5·4	4·4	10·5	74·4	88·5	81·5
Ammonium fluoride fusion‡	—	—	—	—	26·8	86·0	—	—	72·6

*100 g. of ore +200 g. caustic soda, fused and leached with water to remove excess alkali, etc. and residual cake leached with 2 litres of 1.4 *N* sulphuric acid for 1 hr and filtered. Residue used for recovery of Nb and Ta; filtrate used for recovery of U by ion exchange, and U precipitated by ammonia (cake contains 90% U).

†100 g. ore +150 ml. conc. sulphuric acid, heated at 200-210°C. for 1 hr, treated with water and unreacted portion separated.

‡100 g. of ore +300 g. of ammonium fluoride heated to 250°C., leached with water after reaction.

During the extraction by methyl isobutyl ketone (MIBK) all the uranium remained in the aqueous raffinate, which was later precipitated as UF_4 by addition of iron filings or ferrous sulphate.

The digestion studies by all the three methods were repeated on 100 g. scale under the optimum conditions. The results are summarized in Table 1.

Chlorination. The chlorination studies were made on 10 to 100 g. scale in 3 in. diam. silica tube heated externally by a resistance furnace. The powdered ore was converted into pellets by treating with sugar syrup, initially dried at 110°C. in air and later at 400°C. in a current of nitrogen in the furnace itself before introducing chlorine. This was necessary to decompose the sugar into carbon before the chlorination reaction started. Chlorination on a 100 g. scale was done in a vertical furnace, the charge being supported on a porous graphite disc at the bottom. It was found that the mineral could be chlorinated to the extent of about 95 per cent at 500°C. However, under these conditions the volatile niobium and tantalum chlorides were contaminated with uranium and iron which volatilized partly. Experiments were later carried out with the addition of different amounts of sodium chloride to the charge and it was found that all the uranium and iron could be restricted to the nonvolatile portion and purer niobium and tantalum chlorides could be obtained. The optimum conditions were: temperature, 500°C.; ore: carbon:: 10: 3; ore: sodium chloride:: 10: 3; and time, 1 to 1½ hr. Under these conditions, the mineral reacted to the extent of 95 per cent. The volatile portion contained over 90 per cent of the niobium

and tantalum as chlorides, with little contamination of iron and titanium. Titanium contamination was reduced by receiving the niobium and tantalum chlorides in condensers maintained at 140–50°C. The purity of the mixed chlorides was about 98 per cent and the recovery was over 90 per cent.

Uranium in the nonvolatile fraction was mostly in the quadrivalent state. It was extracted by carbonate leaching and recovered by precipitation with sodium hydroxide.

Separation of Niobium and Tantalum by Solvent Extraction. The mixed product of niobium and tantalum obtained in all the processes described earlier were impure, and therefore required further purification. Various methods have been described in literature[1] for the separation and purification of niobium and tantalum. In the present investigation the purification of niobium and tantalum and their separation from each other was affected by liquid-liquid extraction using MIBK (hexone) from aqueous solutions containing hydrofluoric and sulphuric acid mixtures. Initial experiments were carried out in polythene funnels. For large-scale extractions a box-type mixer-settler apparatus, constructed in the laboratory, was employed.

The apparatus, consisted of a two-compartment box of size 10 in. $\times$ 10 in. $\times$ 10 in., and the inner compartment, 6 in. $\times$ 6 in. $\times$ 10 in., made of acid- and solvent-resistant material. The aqueous feed solution from the top and the solvent from the bottom were fed to the inner compartment which served as mixer. The two were thoroughly mixed by an electric stirrer and the mixture was allowed to flow to the outer compartment through a $\frac{1}{2}$ in. hole, where it was separated into two layers which were continuously removed from the outer compartment by two $\frac{1}{2}$ in. exit tubes. This box was capable of handling about 20 litres of mixed phase per hour. By connecting a few boxes of this type in series the whole unit can be made to work continuously for extraction and separation of niobium and tantalum.

Extraction of Niobium and Tantalum from aqueous Solutions. The extractability of niobium and tantalum into the organic phase was determined at different concentrations of hydrofluoric and sulphuric acid. The results (Fig. 1) indicate that the percentage extractions increase with the rise in the concentration of the acid mixture. However, at concentrations greater than $9N$ sulphuric acid $+5N$ hydrofluoric acid the rise in the percentage extraction was comparatively less and therefore this concentration was chosen for further studies.

At constant acidity the per cent extraction also depended on the metal concentration in the aqueous phase, as shown by Fig. 2. At low metal concentrations, even though the percentage extractions were higher, the amount extracted per unit volume of the solvent was less. The variation of the concentration of (Nb, Ta) in the organic phase as a function of the corres-

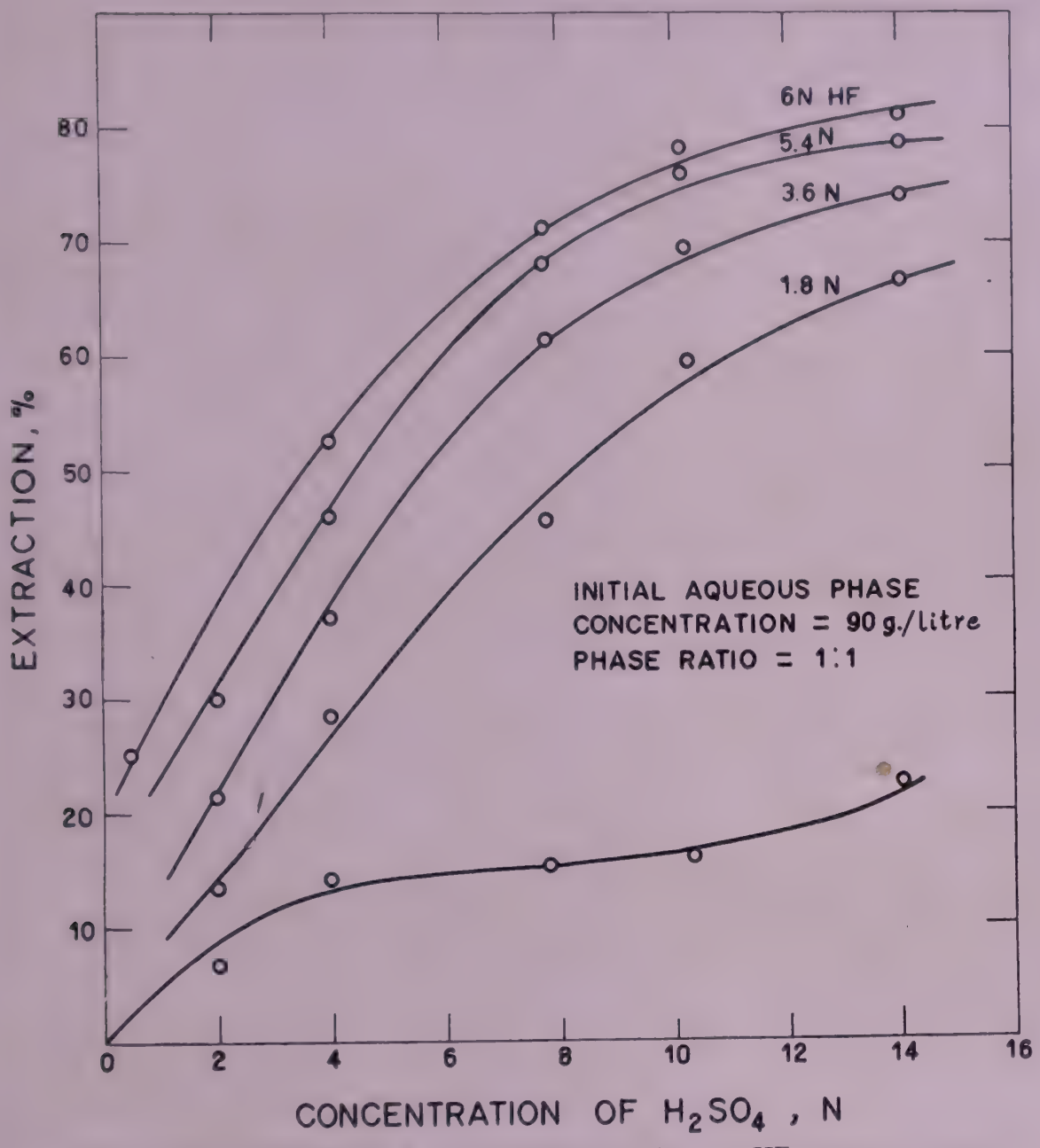

FIG. 1—EXTRACTION OF N_b & T_a AT DIFFERENT H_2SO_4 AND HF CONCENTRATIONS

ponding concentration in the aqueous phase is shown in Fig. 3. It can be seen from the figure that at aqueous concentrations of about 100 g./litre, most of the niobium and tantalum can be transferred into the organic phase by two extractions.

The results of the extraction of niobium and tantalum at various organic to aqueous phase ratios are given in Fig. 4. The amount extracted increased rapidly up to a ratio of 1 · 1, and thereafter the rise in the percentage extraction was little. Hence, the phase ratio was maintained at 1 : 1 in all the experiments.

Separation of Niobium and Tantalum. A solution of niobium and tantalum in 9*N* sulphuric and 5*N* hydrofluoric acid mixture was first

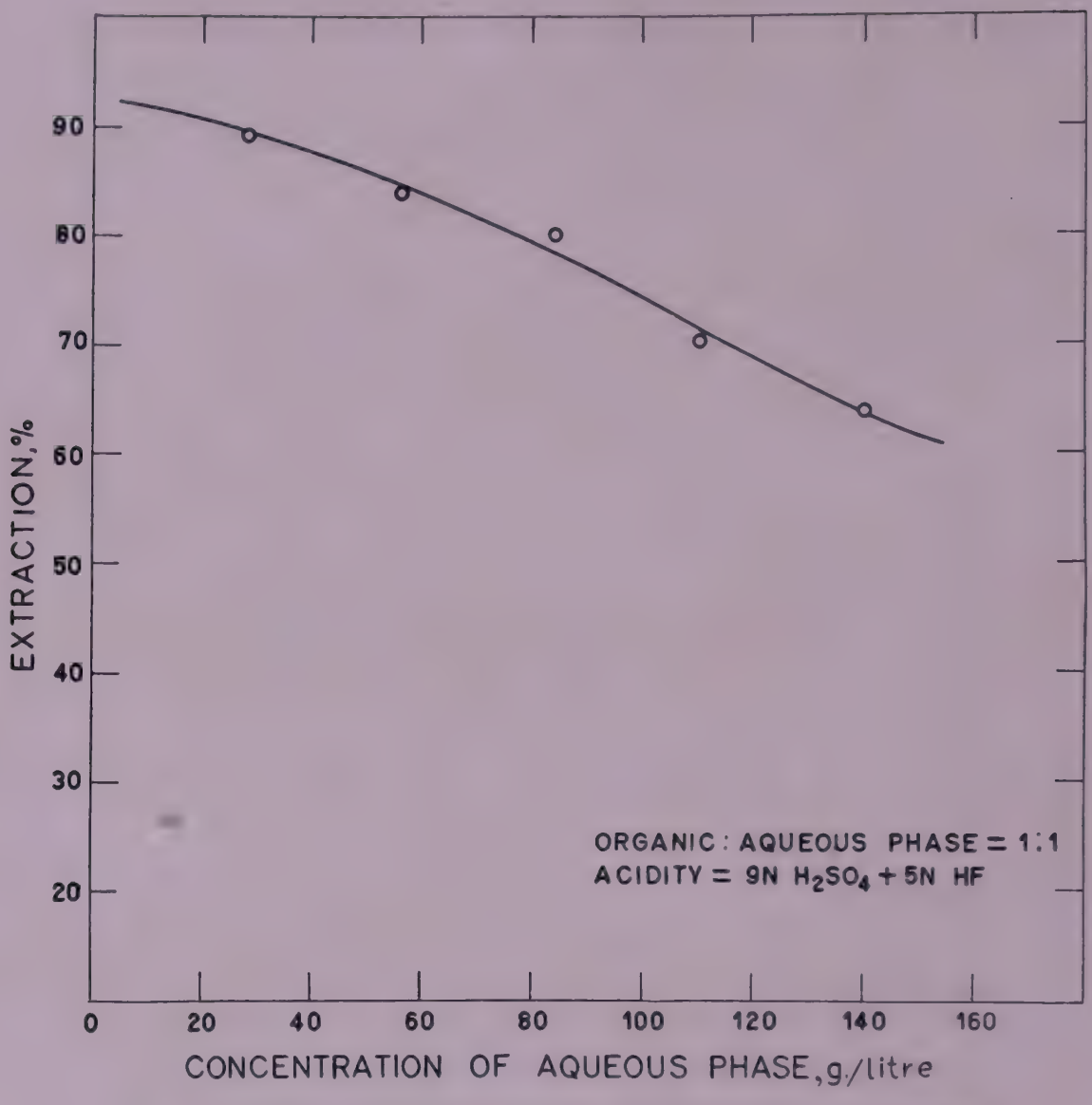

FIG. 2—VARIATION OF EXTRACTION WITH AQUEOUS PHASE CONCENTRATION

extracted with MIBK. This extraction was highly specific and all the impurities were left behind in the aqueous phase. Preliminary experiments indicated that if hydrochloric acid is used in place of sulphuric acid, appreciable amount of iron comes into the organic phase and, therefore, sulphuric acid was preferred in the present investigations. Niobium was back-extracted from the organic phase by washing with an equal volume of 1.*N* sulphuric acid. During this step, appreciable amounts of tantalum also came into the aqueous phase. This was removed from the solution by extracting with half its volume of fresh solvent, which was then added to Stage II. The niobium in the aqueous phase was then precipitated by addition of ammonia, filtered and ignited to the oxide. The product was found to be more than 99·9 per cent pure.

The organic phase from Stage II which contained small amounts of niobium was then removed by scrubbing with a mixture of 1.*N* sulphuric

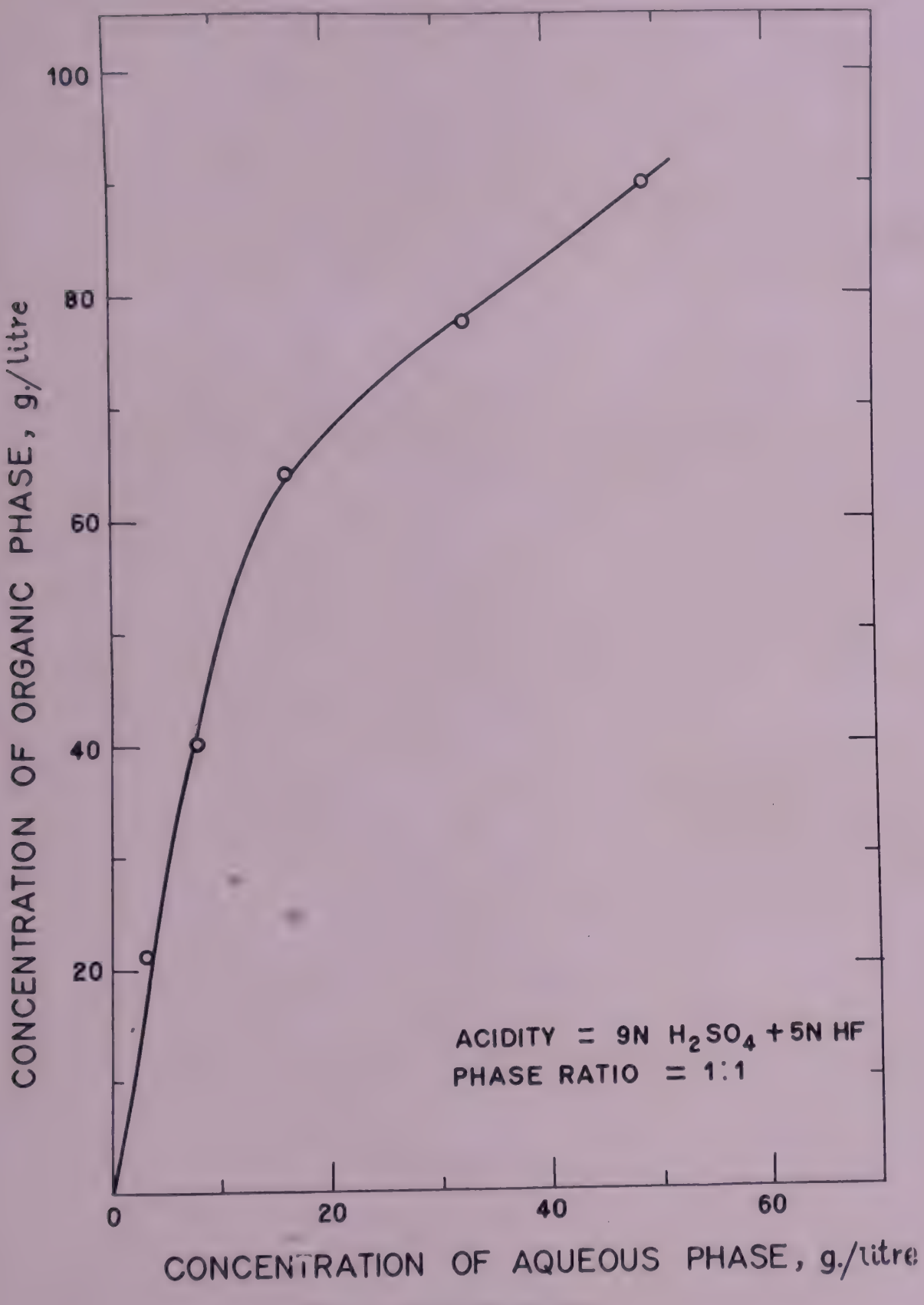

FIG. 3—EQUILIBRIUM DIAGRAM

and 0·5*N* hydrofluoric acids, using one part of the aqueous mixture to every three parts of the organic phase. The aqueous phase obtained here, contain-

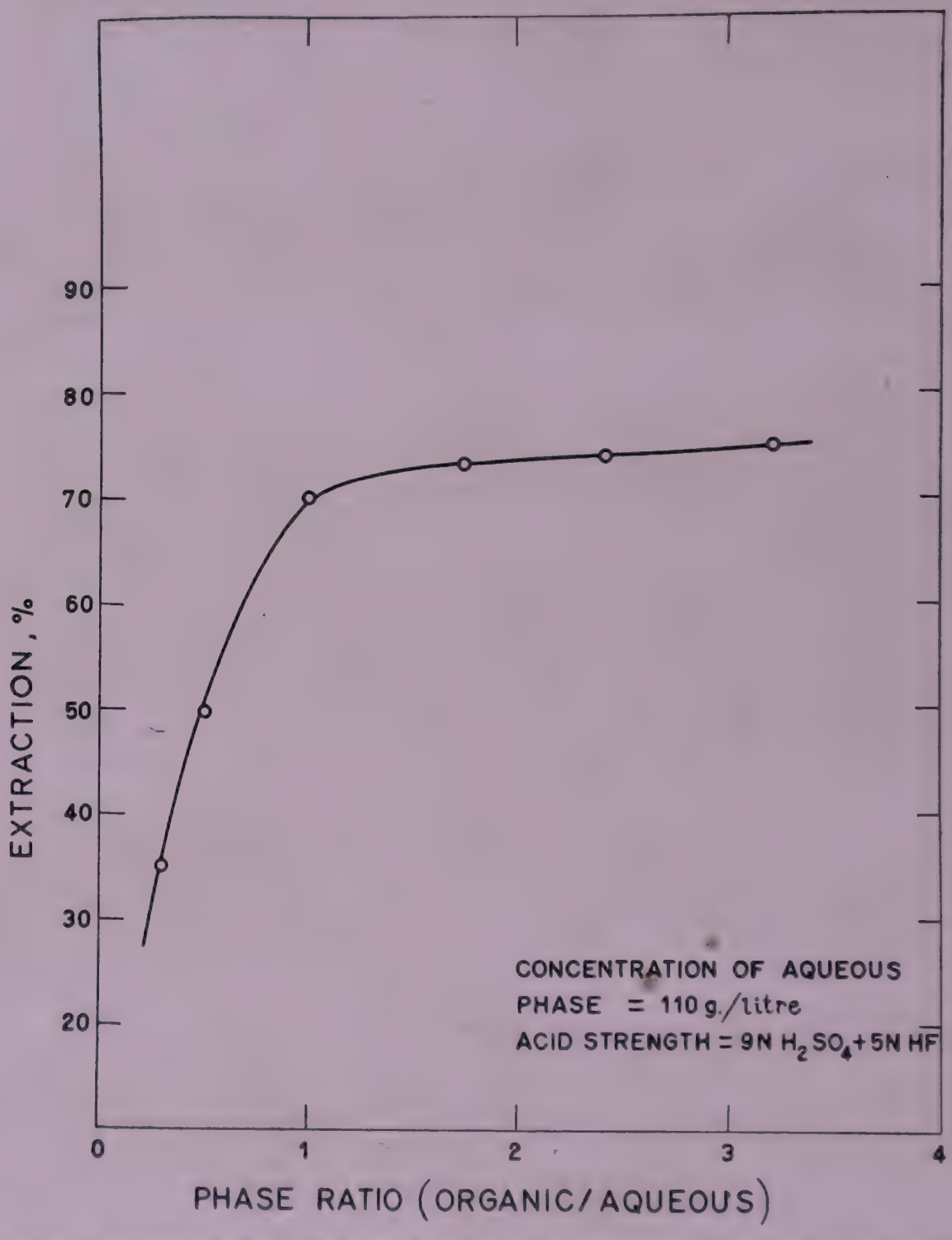

FIG. 4—EXTRACTION OF MIXED EARTH FLUORIDES AT DIFFERENT ORGANIC TO AQUEOUS PHASE RATIOS

ing niobium and tantalum, was added to Stage I. Pure tantalum remaining in the organic phase was stripped by two back extractions with equal volumes of water, precipitated by ammonia, filtered and ignited to the oxide. The product was found to be of more than 99·9 per cent purity. A flow diagram of the complete separation process is given in Fig. 5.

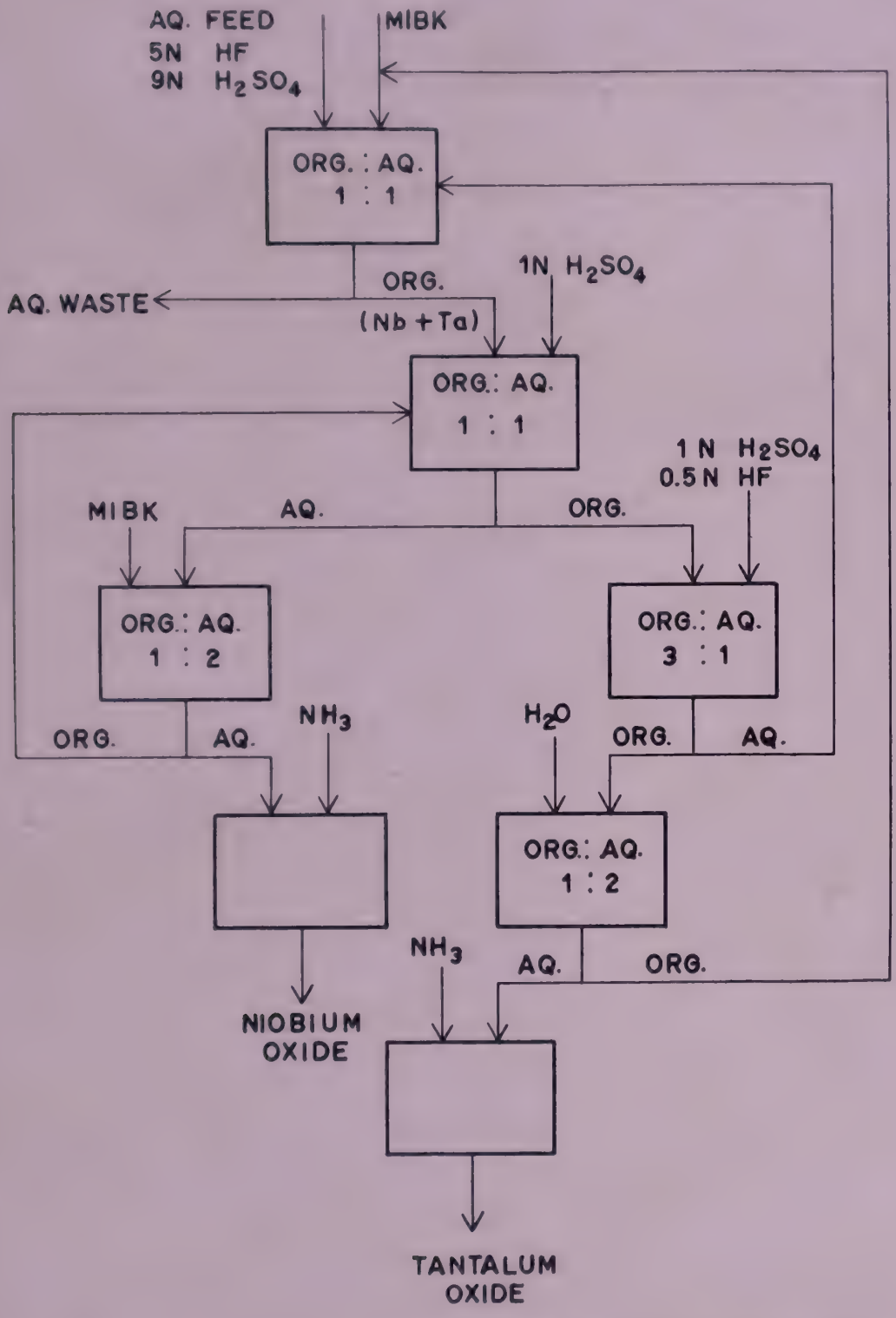

FIG. 5—SEPARATION OF NIOBIUM AND TANTALUM BY LIQUID-LIQUID EXTRACTION

ACKNOWLEDGEMENT

The authors wish to thank Dr G. S. Rao for helpful discussions and Dr J. Shankar for his keen interest in the present work and Dr V. T. Athavale for getting some of the niobium and tantalum samples analysed.

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Preparation of Pectolytic Enzymes

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Laboratory scale preparation of pectolytic enzymes from micro-organisms other than moulds, viz. cultures of *Streptomyces viridochromogenes* **and** *Cryptococcus laurentii* **is described. The actinomycetal preparation is active at alkaline *p*H levels and polygalacturonase elaborated by** *Cr. laurentii* **is active at acid *p*H levels.**

Commercial pectinases have been in use for fruit juice clarification and in wine making for nearly three decades. These preparations, presumably derived from fungal sources, display some pectin methylesterase activity along with their high polygalacturonase activity. Though some species of microorganisms, notably of *Penicillium* and *Aspergillus*, have often been mentioned in connection with the preparation of pectolytic enzymes, no technical details are available as they are all covered by patent rights. Kertesz[1] in his book, *The Pectic Substances*, has however referred to the German preparation 'Filtragol' as a dried bran culture of the mould *Aspergillus aureus* Nakazawa, and the American pectinases, sold under the name 'Pectinols', as mould enzymes obtained from bran cultures by water extraction and reprecipitation with alcohol. The present paper describes the laboratory preparation of pectolytic enzymes from microorganisms other than moulds, viz. cultures of *Streptomyces viridochromogenes* and *Cryptococcus laurentii*. Both these cultures besides representing two different species of microorganisms hitherto undescribed in this connection are capable species in the sense that they can elaborate copious quantities of enzymes in chemically defined media as to hold promise of their exploitation industrially.

MATERIALS, METHODS AND RESULTS

The two organisms investigated for their pectolytic enzymes, viz. *S. viridochromogenes* and *Cr. laurentii* were chosen from 300 odd stock cultures of actinomycetes and yeasts tested for this property. Details of the screening methods, enzyme tests and the cultures examined have been presented elsewhere[2]. Mention may here be made that although both these cultures were isolated by direct methods on routine media and maintained for several generations on pectinless media, they are among the most powerful cultures in our collection.

Medium

The medium employed for harvesting the enzymes of both *S. viridochromogenes* and *Cr. laurentii* has the following percentage composition: $(NH_4)_2SO_4$, 0·05; KH_2PO_4, 0·02; $MgSO_4.7H_2O$, 0·02; $CaCl_2$, 0·01; micronutrient solution*, 0·1 ml.; $Na_2HPO_4.12H_2O$, 0·08; NaCl, 0·005; $FeCl_3$, 0·0001; pectin, 0·5; yeast extract, 0·1; and distilled water to make up the volume. The *p*H of the medium was adjusted to 7·0 before sterilization and it was filled in 200 ml. amounts in Roux bottles for culturing *S. viridochromogenes* and in 100 ml. amounts in 250 or 500 ml. conical flasks for growing *Cr. laurentii*. On autoclaving, the *p*H usually dropped to about 5·0–5·5 and had to be readjusted to about 7·6 for culturing *S. viridochromogenes* and to about 6·6–6·8 for culturing *Cr. laurentii*, using in either case calculated amounts of sterile NaOH solution.

Preparation of crude Enzyme Powders

A suspension of spores of a 7- to 14-day old culture of *S. viridochromogenes* grown on a pectin-mineral solution-yeast extract-liver extract agar medium was made in sterile distilled water and inoculated aseptically into each of the Roux bottles and growth allowed to occur for 5–7 days at room temperature (65–85°F.). At the end of that period the culture filtrate was separated from the mat, adjusted to *p*H 7·0 and cooled to 32°F. The enzyme(s) was then precipitated with cold acetone (20°F.) to a final concentration of 67 per cent (2 volumes). One volume of acetone, employed for precipitating the enzyme(s) in the earlier stages of this work, gave lower yields of the enzyme(s). The floc formed was centrifuged off from the liquid, suspended in distilled water, and dried over anhydrous $CaCl_2$ and NaOH pellets in a vacuum desiccator. The dried material was scraped off from the dish, powdered and stored in a refrigerator. One litre of the culture filtrate yielded about 0·5 g. of crude enzyme powder. This crude preparation, despite the fact that it was accompanied with an appreciable quantity of insoluble material, was comparable in activity to a commercial preparation marketed by the Nutritional Biochemicals Corporation (NBC) with this difference that whereas the NBC product was active at an acid *p*H range, the present preparation could catalyse the reaction optimally at an alkaline *p*H (Fig. 1). The mat was pressed free of the culture fluid, washed with distilled water, followed by acetone and dried as above†. This preparation also possessed considerable polygalacturonase activity thus showing that *S. viridochromogenes* polygalacturonase is both intracellular and extracellular.

The crude enzyme powder from *Cr. laurentii* was prepared by growing the organism on pectin-mineral solution-yeast extract-liver extract agar slants and inoculating it into liquid medium having the same composition

*This solution contained $ZnSO_4 \cdot 7H_2O$, 1·1 g.; $MnSO_4 \cdot H_2O$, 0·5 g.; $CoSO_4$, 0·005 g.; H_3BO_3, 0·005 g.; Na_2MoO_4, 0·2 g.; $CuSO_4 \cdot 5H_2O$, 0·0007 g. per 100 ml.

†For every litre of culture in Roux bottles about a gram of dry mat powder was obtained.

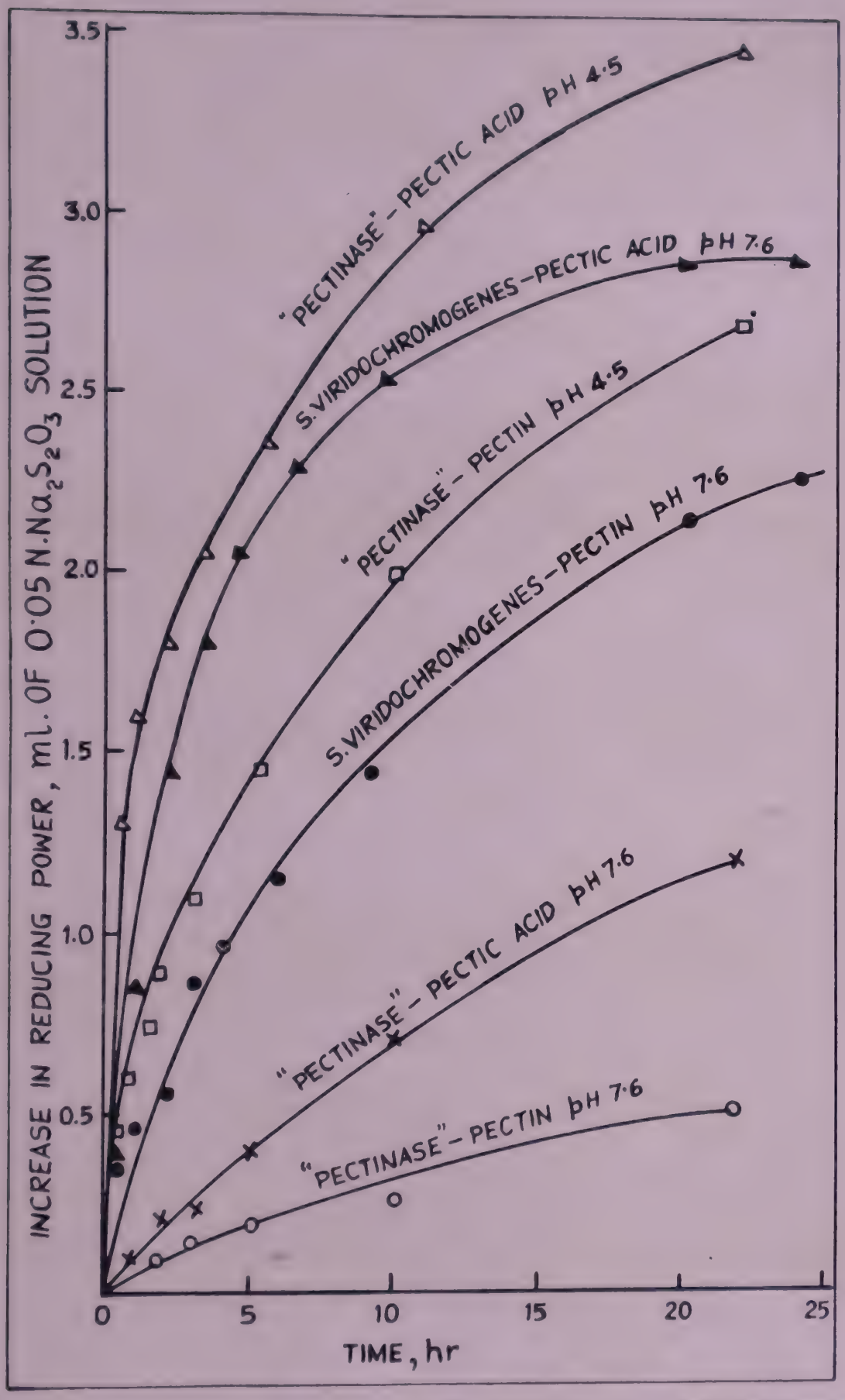

FIG. 1—POLYGALACTURONASE ACTIVITIES OF *S. viridochromogenes* ACETONE-PRECIPITATED ENZYMES AND OF A COMMERCIAL PECTINASE USING BOTH PECTIC ACID AND PECTIN AS SUBSTRATES

as the bulk medium given above. From this growth the bulk medium was inoculated and growth allowed to continue for 3 days with shaking on a rotary shaker (250 r.p.m.), at the end of which the whole culture comprising both intracellular and extracellular enzymes was adjusted to *p*H 5·0, cooled to about 32°F., cold acetone (20°F.) added to a concentration of 50 per cent and the precipitate centrifuged off and obtained as a dried powder in the same manner as for the streptomycete preparation. One litre of culture yielded about a gram of such powder. Attempts to isolate the extracellular enzyme alone have yet to be carried out. This preparation had an optimum activity around *p*H 4·5 (Bilimoria, M. H. & Bhat, J. V., unpublished work).

Measurement of Activity

For measuring this activity, the reducing groups released by the action of the enzyme on a polygalacturonic acid substrate were estimated by the hypoiodite method. To 50 ml. of a 0·5 per cent polygalacturonic acid (Eastman Kodak) substrate were added 10 ml. of the culture filtrate and the enzyme reaction allowed to continue for 24–48 hr. For testing acetone preparations, 5–10 ml. of 0·5–1·0 per cent suspensions thereof were employed. Sodium benzoate and toluene were used to inhibit the growth of contaminating microorganisms.

Factors affecting the Elaboration of Polygalacturonase

Effect of Shaking. With a view to see if shaking of the streptomycete and yeast cultures would accelerate enzyme secretion, two series of cultures, one shaken (on a rotary shaker at 250 r.p.m.) and the other stationary, were simultaneously run and their respective culture filtrates were tested for polygalacturonase activity at different intervals by the hypoiodite method. The results are presented in Figs. 2 and 3. From Fig. 2 it will be seen that in the case of *Cr. laurentii*, shaking results in a rapid increase in the enzyme activity in that on the third day more enzyme was found in the shaken flask than that estimated on the sixth day in the unshaken culture. This probably was due to rapid yeast multiplication. Further shaking however resulted in a loss of enzyme in all probability due to the high *p*H attained by the culture and/or denaturation occurring as a result of increased surface presented by aeration.

In the case of the stationary cultures, on the other hand, the enzyme activity was higher on the sixth day than on the third day, but the level reached on the sixth day by the stationary culture still did not equal that attained on the third day by the shake culture. It is interesting to observe that the rapid elaboration of enzyme in the shake culture of *Cr. laurentii* provides a contrast with the depression in enzyme production witnessed with similar *S. viridochromogenes* culture.

Effect of adding Glucose to the Medium. It was thought that the addition of a sparking agent like a readily available sugar would enable

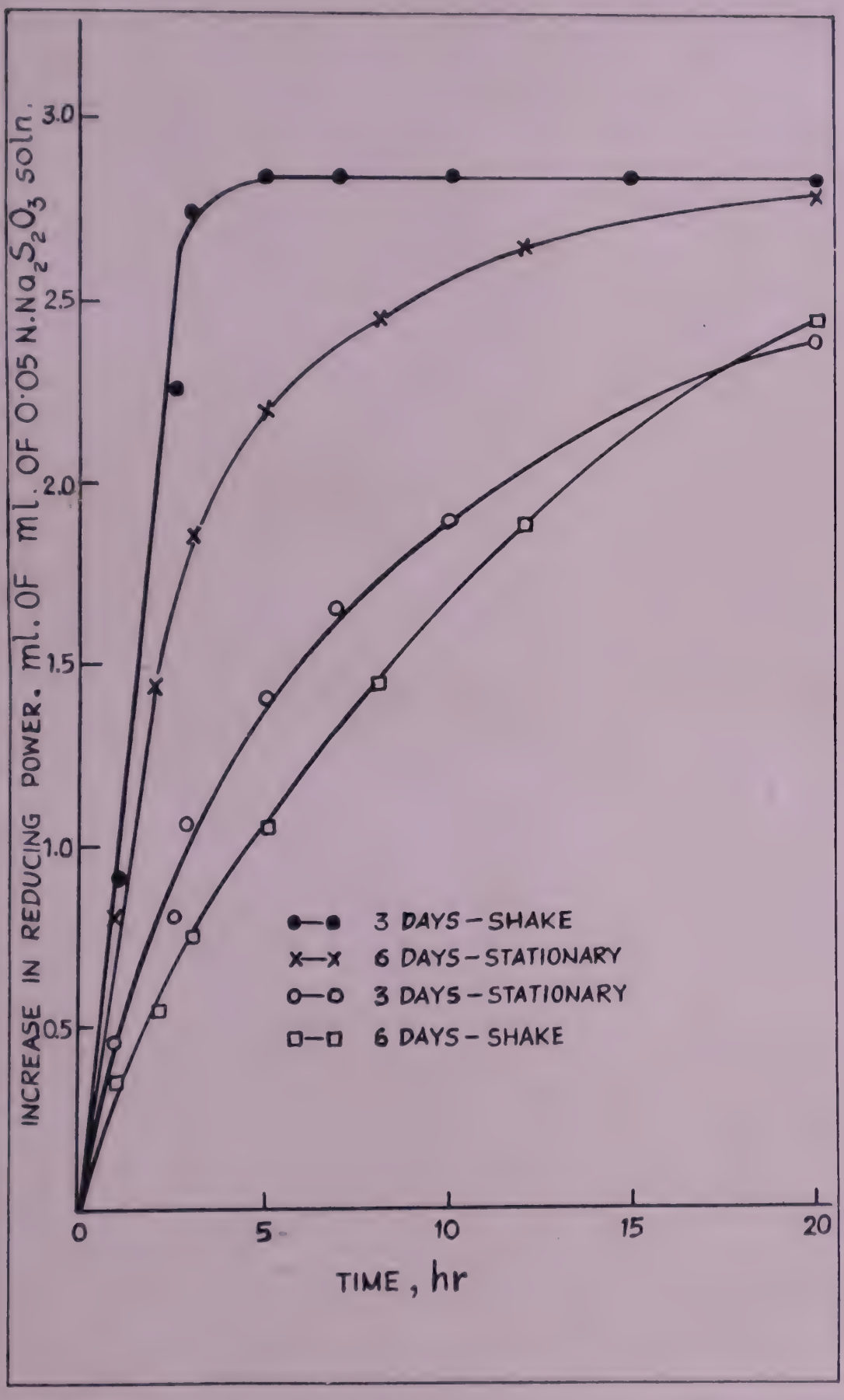

FIG. 2—EFFECT OF SHAKING ON POLYGALACTURONASE PRODUCED BY *Cr. laurentii*

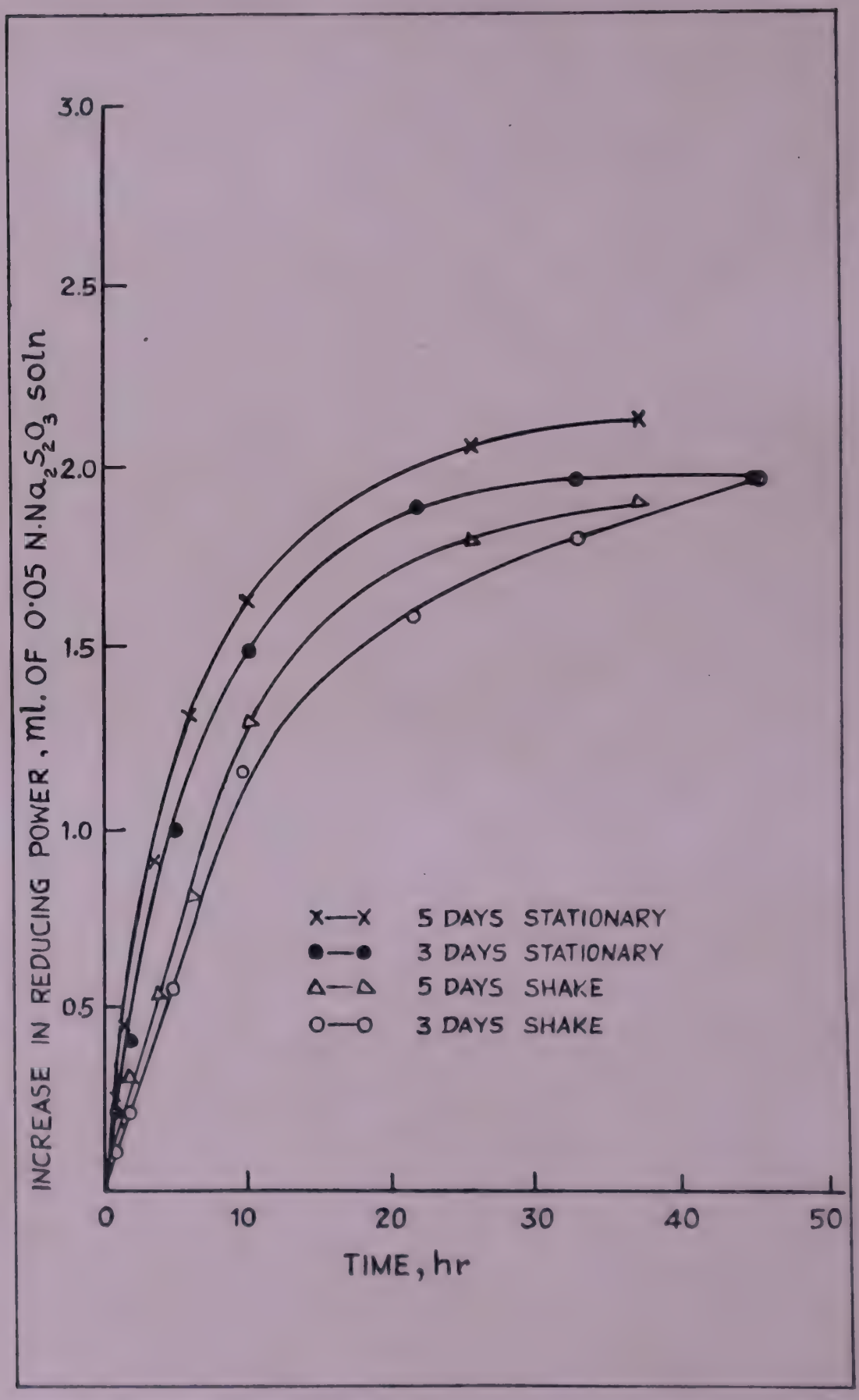

FIG. 3 EFFECT OF SHAKING ON POLYGALACTURONASE PRODUCED BY *S. viridochromogenes*

rapid growth and elaboration of the enzyme. However, in both these cases (*Cr. laurentii* and *S. viridochromogenes*), addition of glucose resulted in a marked decrease in enzyme production (Figs. 4 and 5). The results are not surprising when it is considered that the enzymes elaborated by these microorganisms are adaptively formed, a conclusion reached during subsequent investigations.

Effect of Nitrogen Source and Yeast Extract. The source of nitrogen at the disposal of the streptomycete appeared to influence enzyme production to a large extent. Inorganic sources of nitrogen, such as $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$, NH_4NO_3, $NaNO_3$ and KNO_3, were more favourable for enzyme production than the organic sources including glutamate or peptone (Fig. 6). Casein hydrolysate also resulted in poor enzyme yield. Incorporation of 0·1 per cent yeast extract in the mineral solution-pectin medium, however, resulted in a more rapid growth and better polygalacturonase elaboration than was witnessed in the medium devoid of yeast extract. Some factors in yeast extract appear to promote growth and enzyme elaboration by this culture. Whether the purines and/or pyrimidines or amino acids in quantities inadequate for carbon sources can replace yeast extract is being investigated. Attempts to replace yeast extract by a mixture of ten vitamins of the B complex group resulted in a depression in polygalacturonase elaboration by this streptomycete.

CONCLUSION

The interest of this laboratory in the present investigation on pectic substances stemmed not only from a desire to make available suitable cultures for the preparation of pectic enzymes, but also to attempt a contribution to the more fundamental aspects of microbial degradation of these widely distributed substances. So far as the latter objective is concerned, something definite seems to have been achieved so far [2–5]. As for the former, although crude preparations obtained from the streptomycete and the cryptococcus hold promise of their exploitation industrially, it is difficult to predict their performance under conditions generally given on a mass scale production. However, data collected so far seem to indicate that they would hold good for chemically defined media and as such merit further study on large-scale basis. Under the present context, this is beyond the scope of the investigations in our laboratory. It is significant to note that the simple medium employed renders isolation and purification of the enzyme easier and warrants production of the material economically at the industrial level. It is, at any rate, obvious that as knowledge of the types of enzymes attacking glycosidic bonds in pectic substances increases, the preparation of different enzymes would invariably involve the use of microorganisms other than those already in use, and herein may lie the advantage of using *S. viridochromogenes*

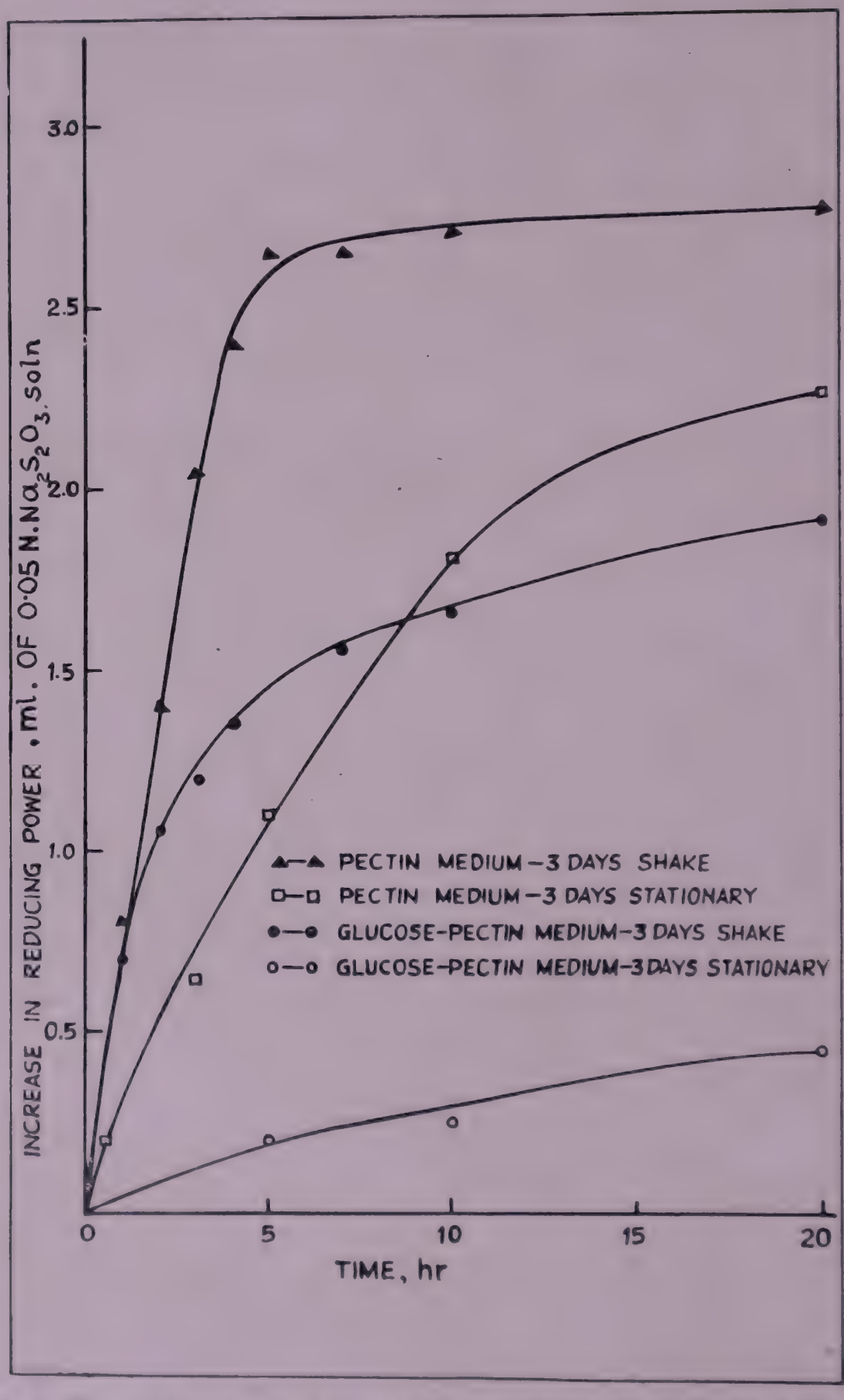

FIG. 4—EFFECT OF INCORPORATING GLUCOSE IN PECTIN MEDIUM AND OF SHAKING ON POLYGALACTURONASE PRODUCED BY *Cr. laurentii*

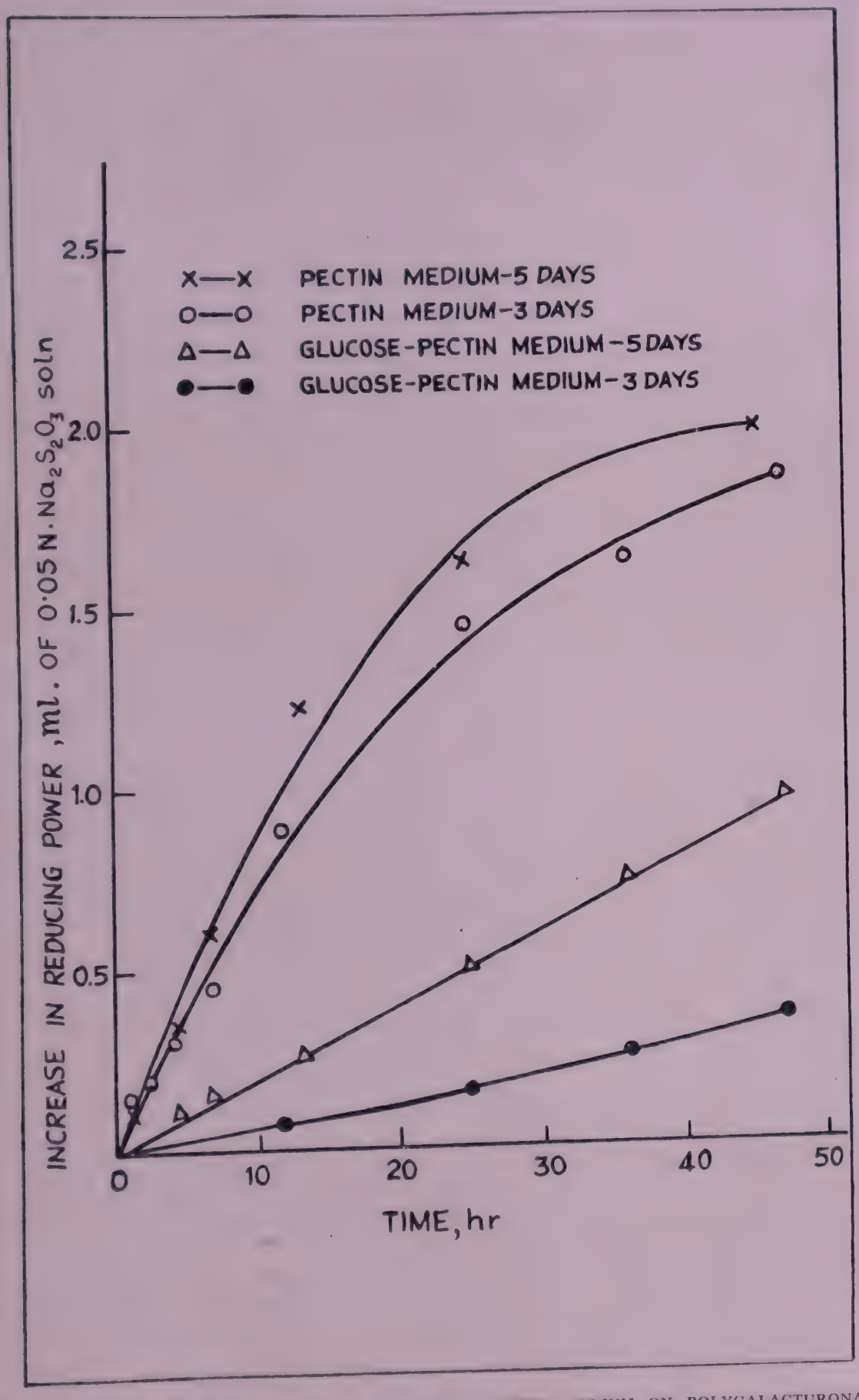

FIG. 5—EFFECT OF INCORPORATING GLUCOSE IN PECTIN MEDIUM ON POLYGALACTURONASE PRODUCED BY *S. viridochromogenes*

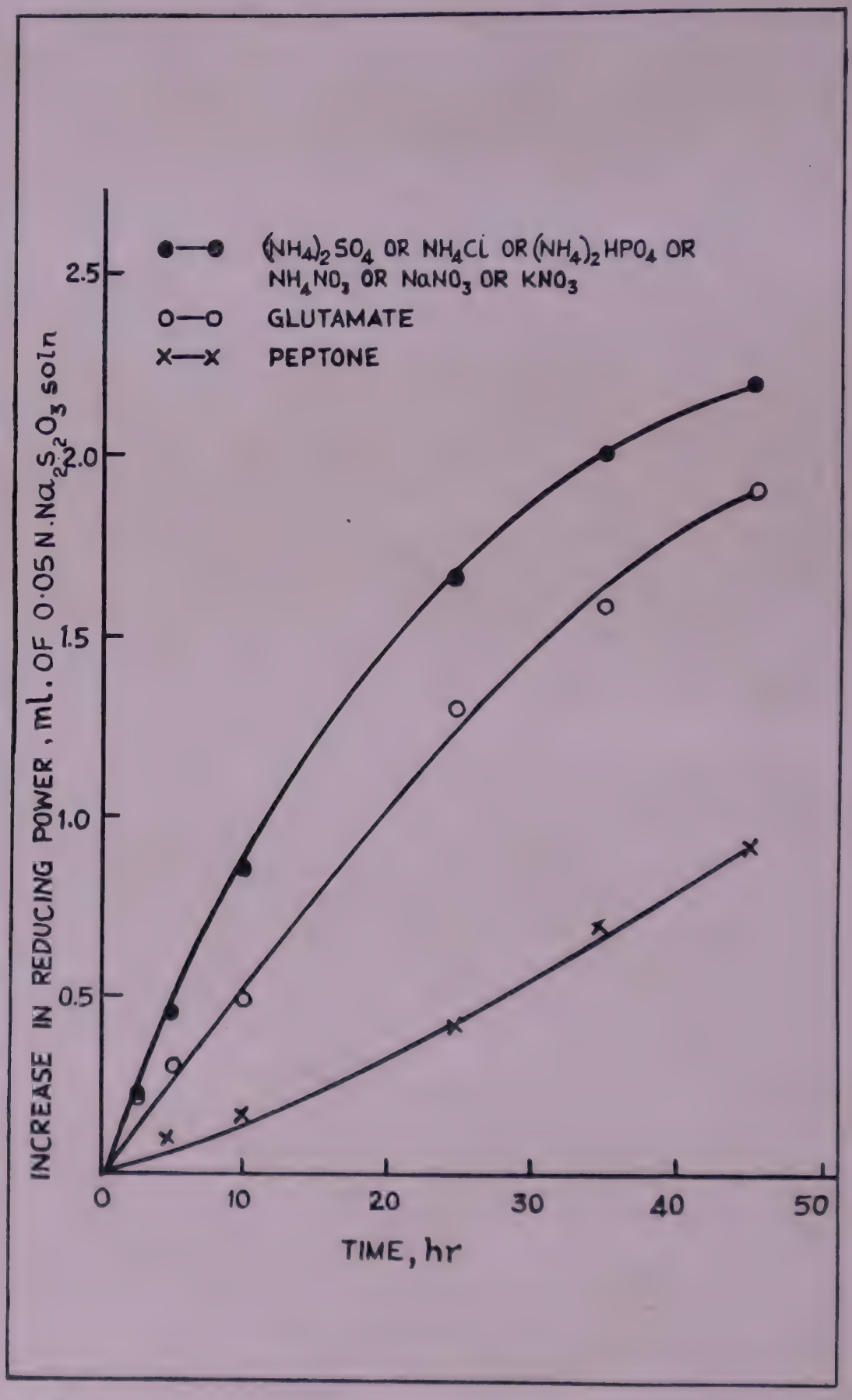

FIG. 6 – EFFECT OF NITROGEN SOURCE ON POLYGALACTURONASE ACTIVITY OF *S. viridochromogenes*

for preparing glycosidase active at alkaline *p*H. Further work on the feasibility of exploiting different groups of microorganisms isolated by the author by the enrichment culture methodology is being pursued with a view to selecting the best enzyme yielding cultures.

Acknowledgement

The author wishes to thank Dr J. V. Bhat for his guidance and Dr S. Bhagavantam, Director, Indian Institute of Science, Bangalore, for his interest in the investigation.

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Kinetics of Coal Carbonization in Fluidized State

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The effect of different operating variables upon carbonization of coal in a fluidized state has been studied, using air as the fluidizing medium. Devolatilization and oxidation have been observed to take place side by side. The rate and extent of carbonization (as given by the rate of devolatilization) and oxidation (as indicated by the increase in mineral matter content) have been found to be enhanced by an increase in the temperature of the reactor as well as that of mass velocity of air.

On the basis of the experimental results, a mechanism for carbonization has been proposed. The carbonization has been found to follow a two-stage process as in the case of carbonization of coking coal, i.e. first stage of plastic state formation followed by second stage of coking and devolatilization. The rate can be expressed with the help of an equation.

Fluidized bed carbonization of coal has been investigated by many workers. The investigations have been carried out mainly on the different aspects of the process with major emphasis on the quality of the products obtained in the temperature range of 500–800°C., on laboratory as well as full plant scale. Among the large-scale investigations, mention may be made of the work carried out by Pittsburg Consolidation Co.[1], Institute of Gas Technology[2], U.S.A. and Imperial Chemical Industries[3], U.K. The three-stage technique of preoxidation, carbonization and gasification has been followed by some workers[4–7]. It has been found that while using coking coal preoxidation is necessary for destroying the coking power of coal[8, 9].

As a medium of fluidization, the use of air, oxygen, nitrogen and steam has been reported[10–12]. The investigations of Lahiri *et al.*[12] show that during the low temperature carbonization of non-caking Indian coals about 73 per cent of volatile matter can be removed, the calorific value of the gas to be 160 B.t.u./cu. ft. The particles of the char have been observed to have an increased size and decreased bulk density. Several other techniques relating to various modifications of the process have been reported and are mostly covered by patents[13–15].

Stone *et al.*[16] have found that the composition and rate of evolution of gases from coal during fluidized bed carbonization are the same as those during heating of coal during coking in a fixed bed. The process proceeds in three stages: the first stage consisting of evolution of loosely bound

moisture, carbon monoxide and carbon dioxide followed by a rapid second stage of evolution of gases and the third stage of slow degassing.

But no attempt has been made so far to study the kinetics of carbonization. The object of the present work has been to investigate the mechanism and kinetics of carbonization in a fluidized bed using air as the fluidizing medium and to find out the effect of the different operating variables on carbonization.

EXPERIMENTAL PROCEDURE

The set-up used for carbonization studies is shown in Fig. 1. Coal is fed from the reservoir 'S' into the nozzle 'N' by means of the variable speed screw-feeder 'F', the latter being driven by a motor. Compressed air, after being purified in an oil scrubber and a silica gel tower, is metered by an orifice meter and admitted at the bottom of the fluidizer 'R'. The fluidizer consists of $2\frac{1}{4}$ in. internal diameter stainless steel column inside which a 5/8 in. outer diameter cylindrical baffle is fixed centrally. The total height of the fluidizer is 3 ft. The bottom of the fluidizer is connected to the nozzle assembly 'N' by means of the fitting 'B' and the top is flanged. Thermocouple wells are provided for measuring the temperature of the bed. Through the upper thermocouple well a connection is made to withdraw the product char at definite intervals of time by applying suction. Metal wall temperatures are recorded by thermocouples Tw_1, Tw_2 and Tw_3 and their junctions are welded to the metal surface. The gaseous materials leave the top of the fluidizer and enter the cyclone where particles of char are recovered.

The fluidizer is heated electrically from outside by means of Kanthal-A wire. Heating is done in two sections—each section being made of mild steel (M.S.) frames of the size 18 in. $\times 4\frac{1}{2}$in. $\times 1\frac{1}{2}$in. and arranged in the form of a square. Heating coils are fitted into the grooves of the refractory tiles which are fixed to the frame. The ends of the coil are connected to $\frac{1}{4}$ in. M.S. bolts passing through the tiles and these serve as terminals for power input. Details of the heating device have been shown in Fig. 2. Variac transformers are used to regulate the power input and the e.m.f. generated by thermocouple is measured with a potentiometer.

The heaters are put on and after some time the air supply is started. When steady state is attained, coal is fed into the fluidizer by opening the valve V_1 and operating the screw-feeder. The solids flow is stopped after sometime and the heat input is regulated so as to get a uniform bed temperature. The amount of material retained in the fluidizer will be under batch fluidizer condition. Samples of char are withdrawn from the fluidizer at regular intervals of time for subsequent analysis.

Experiments were conducted with the bed temperatures of 810, 885, 925, 975 and 1020°F. and with the air mass velocity of 844, 1042 and 1172 lb./hr/sq. ft.

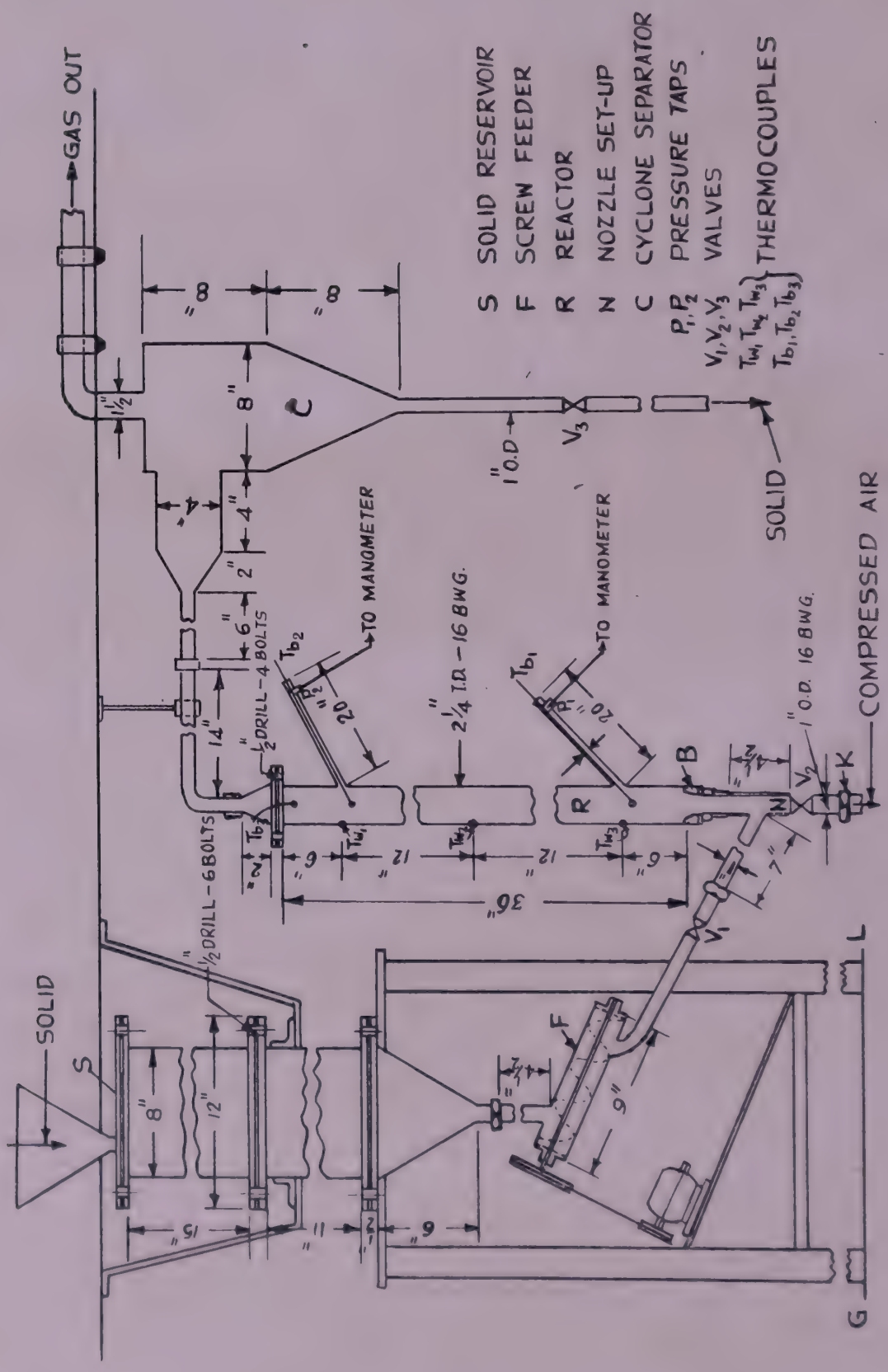


FIG. 1—SET-UP FOR FLUIDIZATION STUDIES

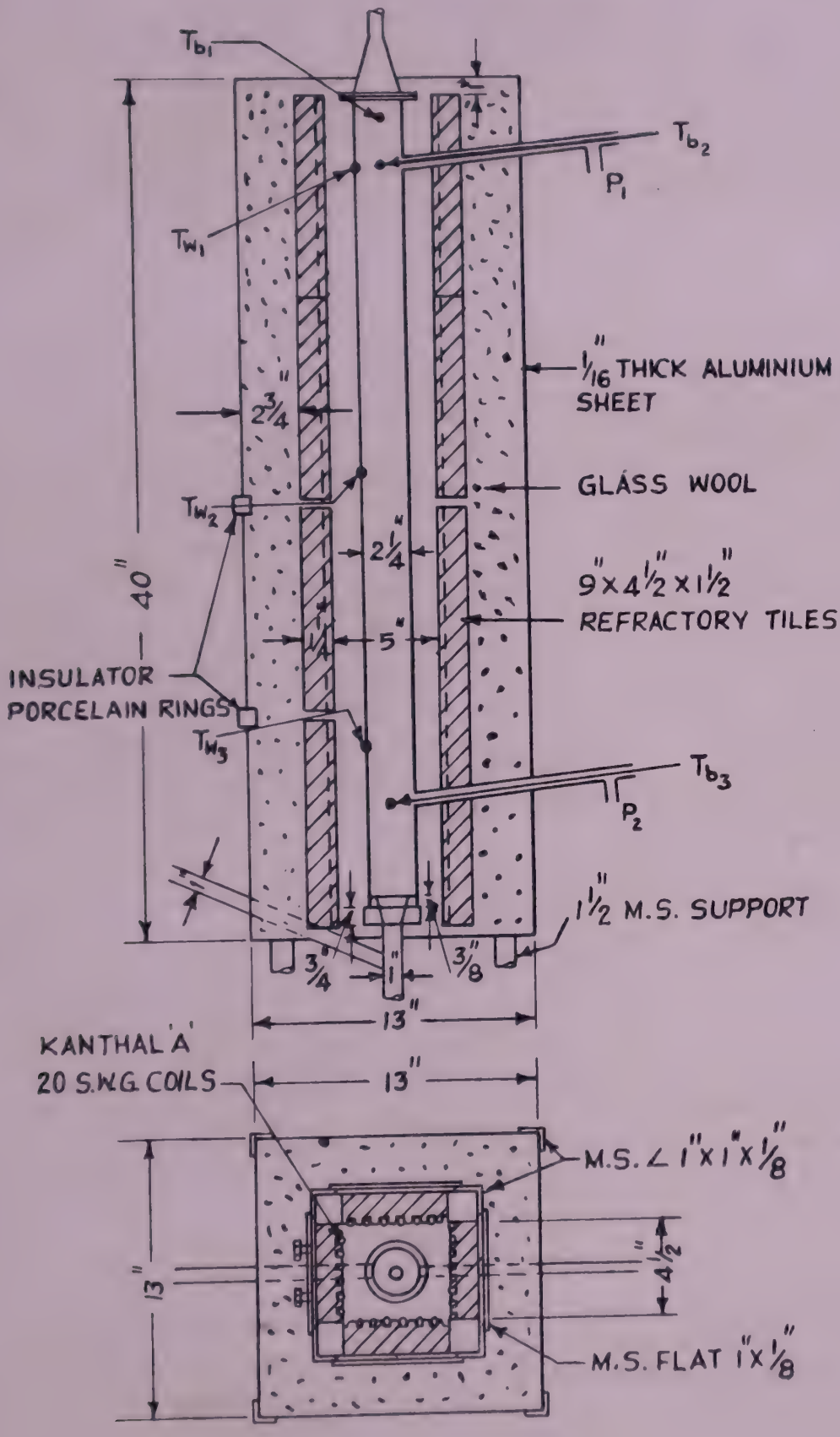


FIG. 2—DETAILS OF EXTERNAL HEATING DEVICE

The extent of carbonization reaction has been determined from the degree of devolatilization and the residual volatile matter content of the char has been used as an index for this purpose.

RESULTS AND DISCUSSION

Particulars regarding the feed coal are given in Table 1. Analyses of the char obtained under the different operating conditions are given in Tables 2, 2a and 2b. The increase in the ash content of the char has

TABLE 1—PARTICULARS OF FEED COAL

(*Batch fluidizer: length, 3 ft; inner diam., 2¼ in.; and outer diam. of baffle, 5/8 in.*)

Particle size, ft		0·001969
Analysis	vol. matter, %	23·46
	ash, %	28·92
Fluidizing medium		Air
Mass velocities of fluidizing medium, lb./hr/sq. ft		844,1042 & 1172
Bed temperatures, °F.		810, 885, 925 975 & 1020

TABLE 2—ANALYSIS OF CHAR OBTAINED UNDER DIFFERENT OPERATING CONDITIONS

(*Fluidizer: inner diam., 2¼ in. and outer diam. of baffle, 5/8 in.; air mass velocity, 844 lb./hr/sq.ft; and coal,* $D_p = 0{\cdot}001969$ *ft*)

Av. bed temp. °F.	Time min.	Char analysis*		Vol. matter loss %	Combustible matter loss %	Av. time min.	Rate of vol. matter loss per min.
		Vol. matter %	Ash %				
885	1·0	22·55	29·76	6·63	4·04	0·50	6·63
885	1·5	21·56	30·68	13·46	8·14	1·25	13·64
885	2·0	20·55	31·27	19·09	10·66	1·75	11·28
885	3·0	17·42	33·36	35·70	18·73	2·50	16·61
885	3·5	13·41	36·78	55·10	28·94	3·25	38·80
885	4·0	9·82	40·56	70·30	40·40	3·75	30·40
975	1·0	20·74	29·88	14·60	4·60	0·50	18·60
975	1·5	19·93	31·92	23·60	13·26	1·25	18·60
975	2·0	16·56	35·12	41·80	24·80	1·75	36·40
975	2·5	14·16	38·86	55·10	36·15	2·25	26·60
975	3·25	8·14	47·53	79·30	55·20	2·87	32·20

*Dry basis

TABLE 2a –ANALYSIS OF CHAR OBTAINED UNDER DIFFERENT OPERATING CONDITIONS

(*Air mass velocity*, 1042 *lb./hr/sq. ft*)

Av. bed temp. °F.	Time min.	Char analysis*		Vol. matter loss %	Combustible matter loss %	Av. time min.	Rate of vol. matter loss per min.
		Vol. matter %	Ash %				
885	1·0	22·00	29·72	8·90	3·92	0·50	8·90
885	1·5	20·97	31·13	16·96	9·97	1·25	16·12
885	2·0	19·98	33·22	25·80	18·25	1·75	17·68
885	2·5	17·37	35·36	36·00	26·10	2·25	20·40
885	3·0	13·63	39·49	57·40	37·80	2·75	42·80
885	3·5	10·04	44·69	72·30	49·60	3·25	29·80
925	0·5	23·04	29·10	2·50	0·95	0·25	00·50
925	1·0	21·38	29·87	11·85	4·58	0·75	19·30
925	1·5	19·10	32·03	26·55	13·74	1·25	29·40
925	2·0	13·48	34·55	51·90	23·15	1·75	48·70
975	0·5	22·14	29·60	7·95	3·30	0·25	15·90
975	1·0	20·50	30·10	16·20	5·80	0·75	16·50
975	1·5	15·60	32·46	40·80	15·35	1·25	49·20
975	2·0	10·83	36·72	63·70	29·90	1·75	45·80

*Dry basis

been found to be more than that which can be explained by the loss of volatile matter alone. This shows that some combustion is taking place during the process. Additional evidence in support of combustion was obtained in some preliminary runs, in which it was found that the temperature of the bed went up during the process and also the percentage of carbon dioxide was considerably high. The total loss in combustible matter (including volatile matter and carbon) has been calculated on the basis of the increase in ash content (Table 3).

The effect of different bed temperatures and different gas mass velocities upon the residual volatile matter content of the char can be seen from Figs. 3,3a & 3b; and 4 & 4a respectively. The percentage loss in volatile matter and the rate of degasification under different operating conditions can be observed from Figs. 5,5a & 5b; 6 & 6a; 7,7a & 7b; and 8 & 8a. Similarly, the per cent loss in combustible matter using different bed tem-

peratures and different mass velocities has been shown in Figs. 9,9a & 9b; and 10 & 10a respectively. It can be seen from the above data and figures that the higher the bed temperature, the greater is the evolution of the gas. At a particular bed temperature, it is seen that more volatile matter

TABLE 2b—ANALYSIS OF CHAR OBTAINED UNDER DIFFERENT OPERATING CONDITIONS

(*Air mass velocity*, 1172 *lb./hr/sq. ft*)

Av. bed temp. °F.	Time min.	Char analysis*		Vol. matter loss %	Combustible matter loss %	Av. time min.	Rate of vol. matter loss per min.
		Vol. matter %	Ash %				
810	1·0	23·20	29·05	1·70	—	0·50	1·70
810	1·5	22·30	29·83	7·85	4·40	1·25	12·30
810	2·0	21·50	30·65	13·85	8·14	1·75	12·00
810	2·5	20·10	32·68	22·70	14·00	2·25	17·70
810	3·0	17·25	35·41	40·00	25·30	2·75	34·60
810	3·5	14·65	38·42	52·60	33·90	3·25	25·20
810	4·42	8·36	47·36	78·30	54·70	—	—
885	1·0	21·72	29·41	8·95	2·37	0·50	8·95
885	1·5	20·70	30·57	16·54	7·67	1·25	15·18
885	2·0	19·15	32·15	26·75	14·34	1·75	20·42
885	2·5	16·06	34·47	42·70	22·70	2·25	31·90
885	3·0	12·65	37·13	58·20	31·10	2·75	31·00
975	1·0	19·54	30·20	20·23	6·06	0·50	6·06
975	1·5	16·36	36·36	44·57	28·62	1·25	24·68
975	2·0	12·31	43·51	65·18	47·21	1·75	41·22
1020	0·5	21·11	29·86	12·95	4·51	0·25	25·90
1020	1·0	17·78	32·14	32·09	14·17	0·75	38·28
1020	1·5	13·17	39·58	59·03	37·94	1·25	53·88
1020	2·0	8·50	48·21	78·29	56·33	1·75	38·52

*Dry basis

TABLE 3—TOTAL LOSS IN COMBUSTIBLE MATTER INCLUDING VOLATILE MATTER AND CARBON

(*Bed temp.*, 885°*F.*)

Mass velocity *lb./hr/sq. ft*	Time *min.*	Loss of vol. matter per 100 g. of coal *g.*	Loss of combustibles per 100 g. of coal *g.*	Loss due to oxidation per 100 g. of coal *g.*
844	1·0	2·51	2·08	0·57
844	1·5	3·16	5·68	2·52
844	2·0	4·46	7·58	3·12
844	3·0	8·06	13·28	5·22
844	3·5	12·91	21·38	8·47
844	4·0	16·46	28·58	12·12
1042	1·0	2·06	2·48	0·42
1042	1·5	4·01	7·48	3·47
1042	2·0	6·06	12·98	6·92
1042	2·5	12·52	18·18	5·66
1042	3·0	13·70	27·38	13·68
1042	3·5	16·75	35·18	18·43

and combustible matter are lost as the gas mass velocity is increased. This may be attributed to the fact that at higher mass velocity of air, there is probably greater chance of oxidation reactions taking place. This may result in a local rise in temperature, with the consequent evolution of more volatile matter. From Figs. 7 and 8 it may be seen that the loss in volatile matter takes place in three different stages:

(i) **Induction Period.** This period corresponds to a very slow rate of degassing. This is probably due to the fact that just after the injection into the reactor, it takes some time for the material to be heated up to the degassing temperature. This results in a slower rate of degassing in the initial period.

(ii) **Faster Rate Period.** It can be seen that the rate of degassing increases and reaches a maximum value depending upon the temperature and gas mass velocity. With a rise of the bed temperature and an increase in the gas mass velocity there is a tendency for the maximum rate to shift towards the origin, i.e. less time is required to reach the maximum rate.

(iii) **Slower Degassing Rate.** The rate of evolution of gas gradually falls off during this period.

Van Krevelen and his collaborators[17,18] have studied the kinetics of coal carbonization in the case of coking coal. They have shown that when

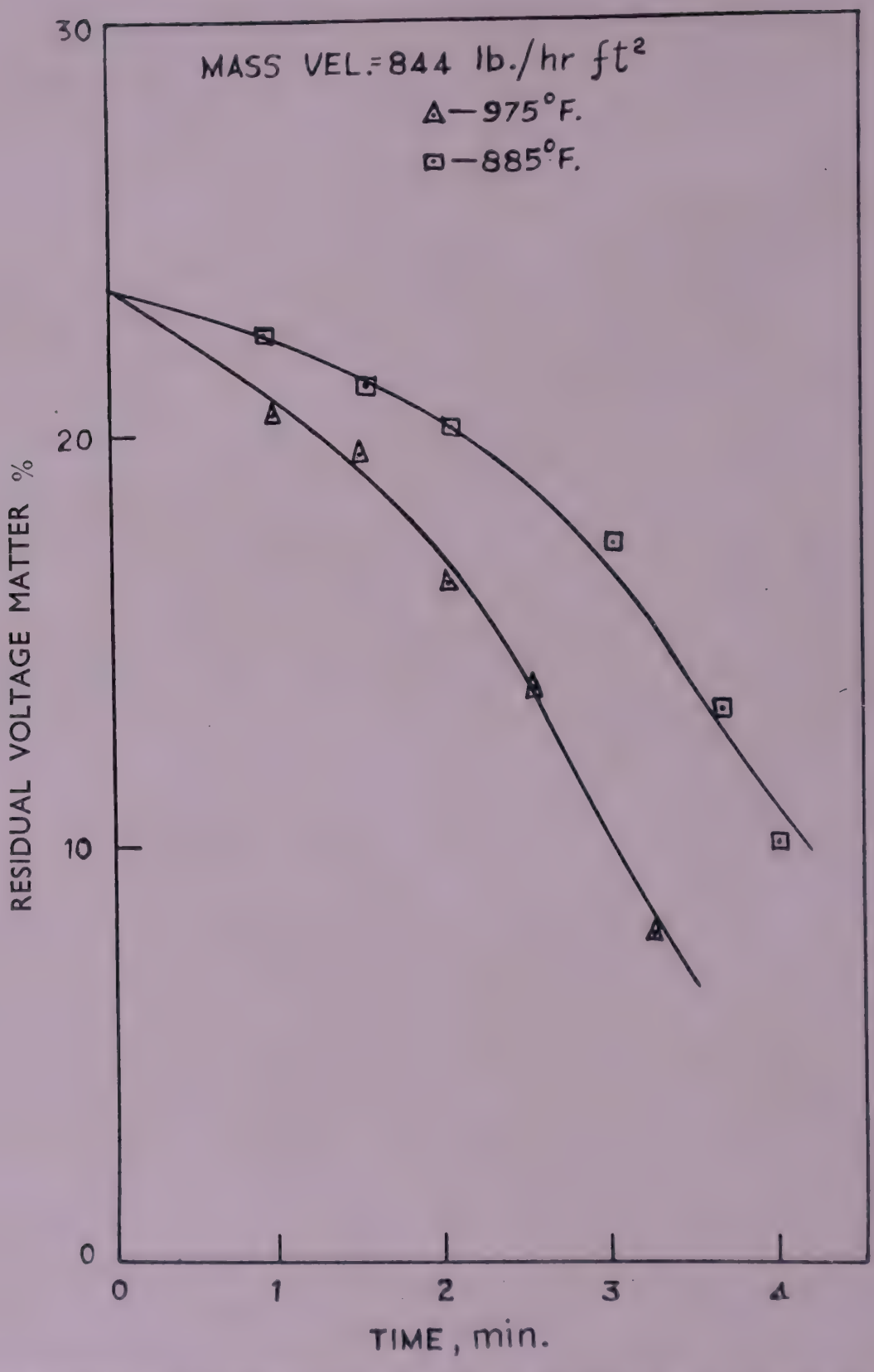


FIG 3—EFFECT OF BED TEMPERATURE AND TIME OF RESIDENCE ON DECREASE IN VOLATILE MATTER

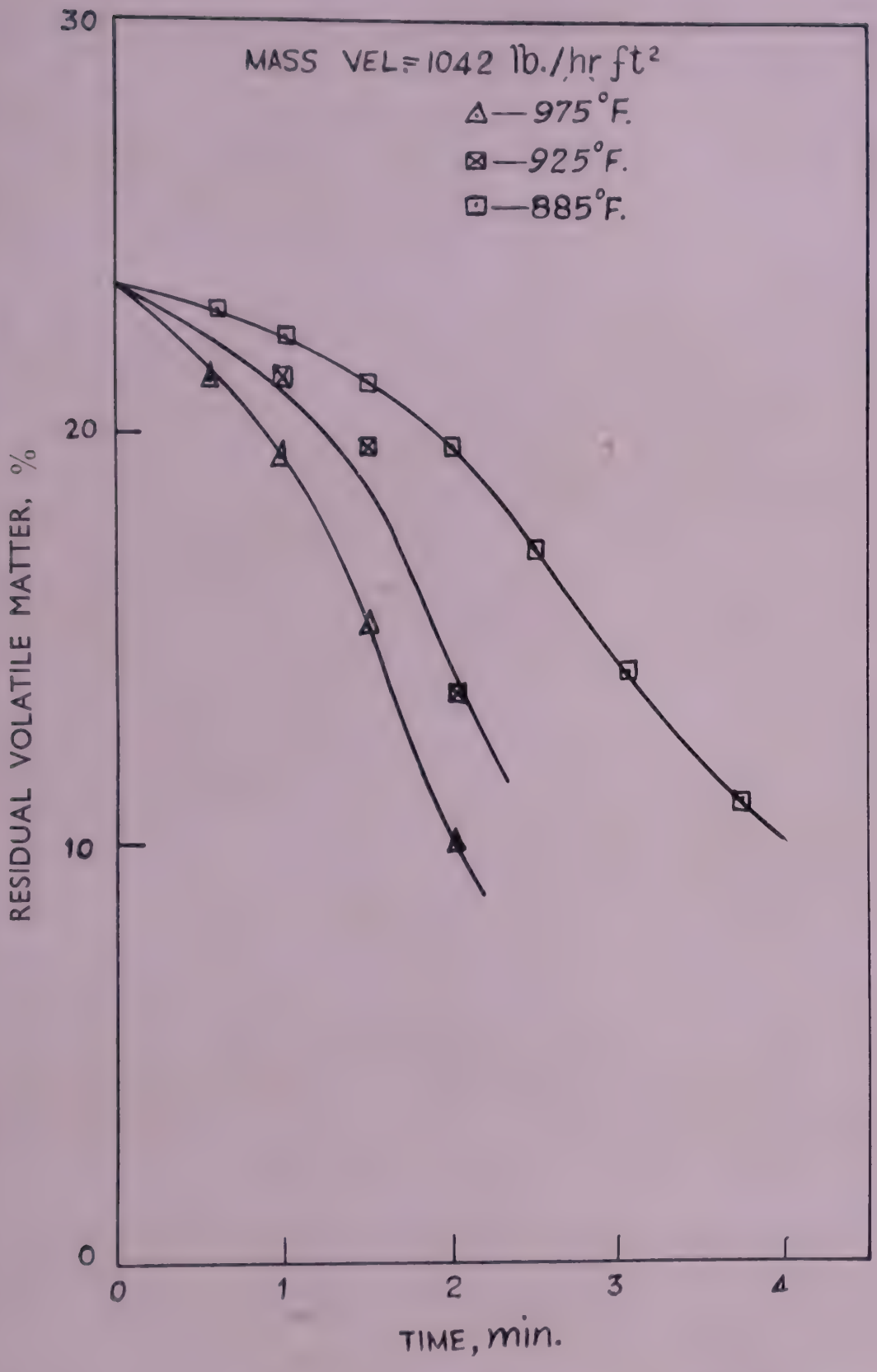


FIG. 3a—EFFECT OF BED TEMPERATURE AND TIME OF RESIDENCE ON DECREASE IN VOLATILE MATTER

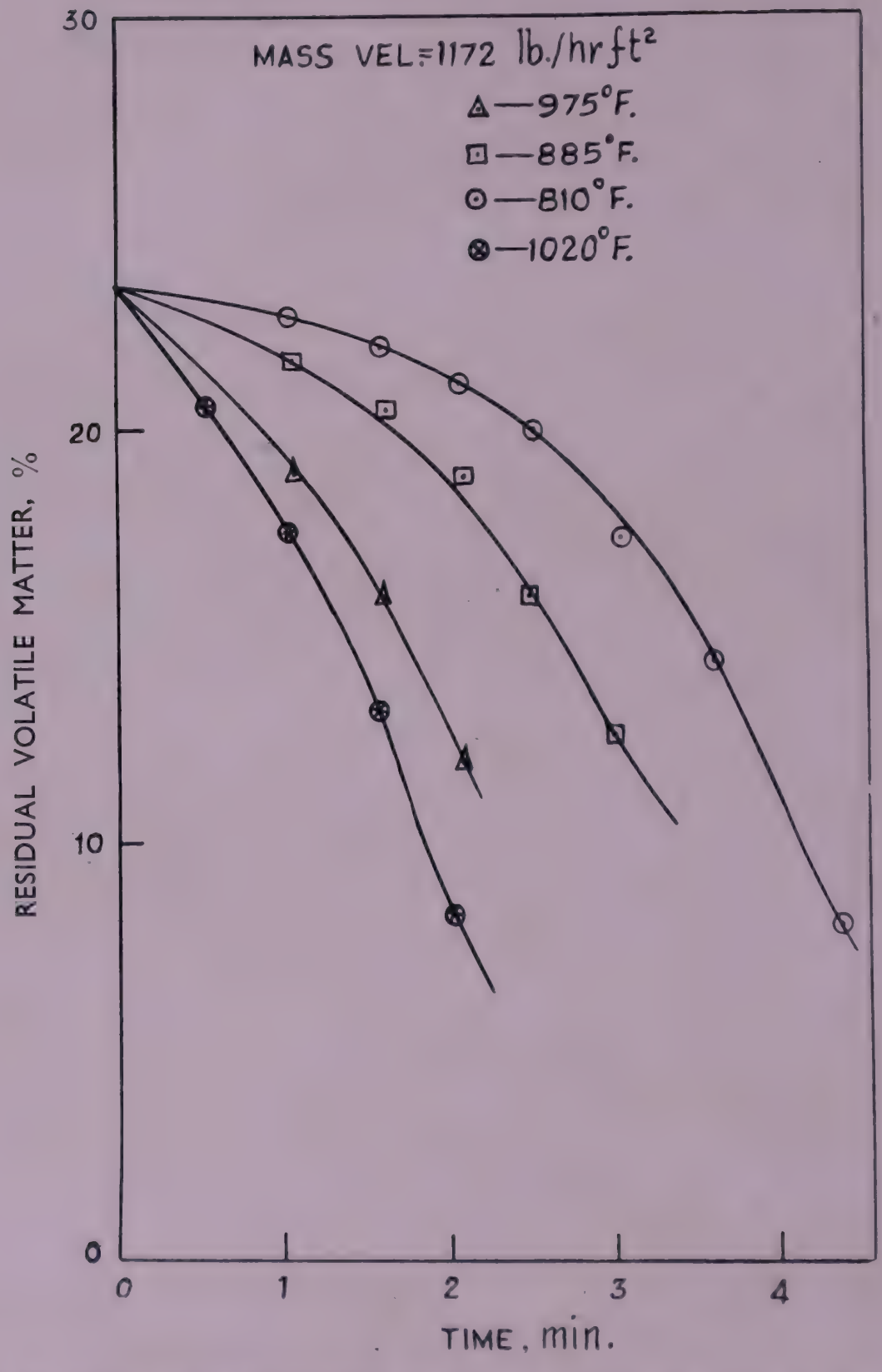


FIG. 3b—EFFECT OF BED TEMPERATURE AND TIME OF RESIDENCE ON DECREASE IN VOLATILE MATTER

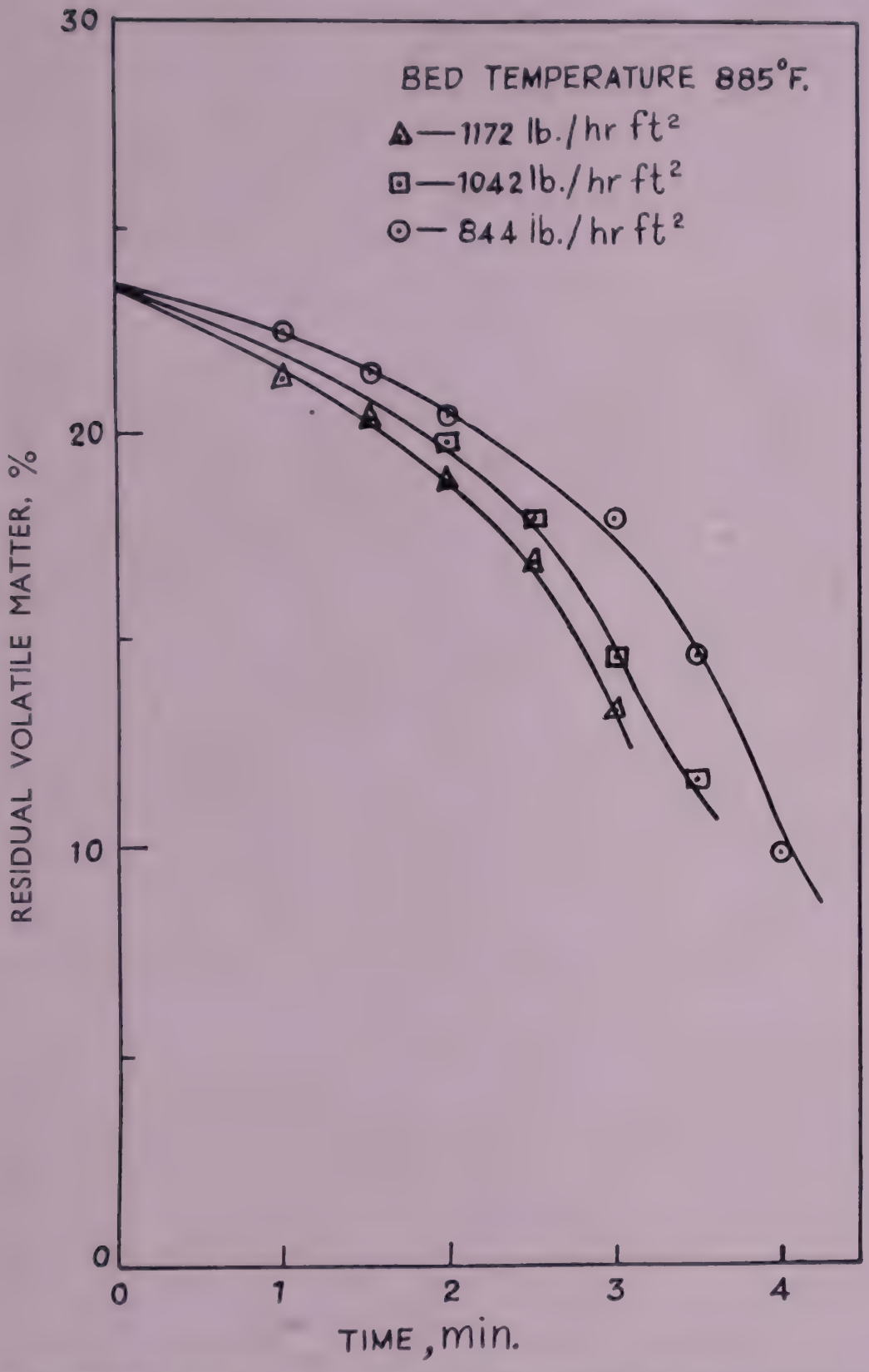


FIG. 4—EFFECT OF MASS VELOCITY AND TIME OF RESIDENCE ON DECREASE IN VOLATILE MATTER

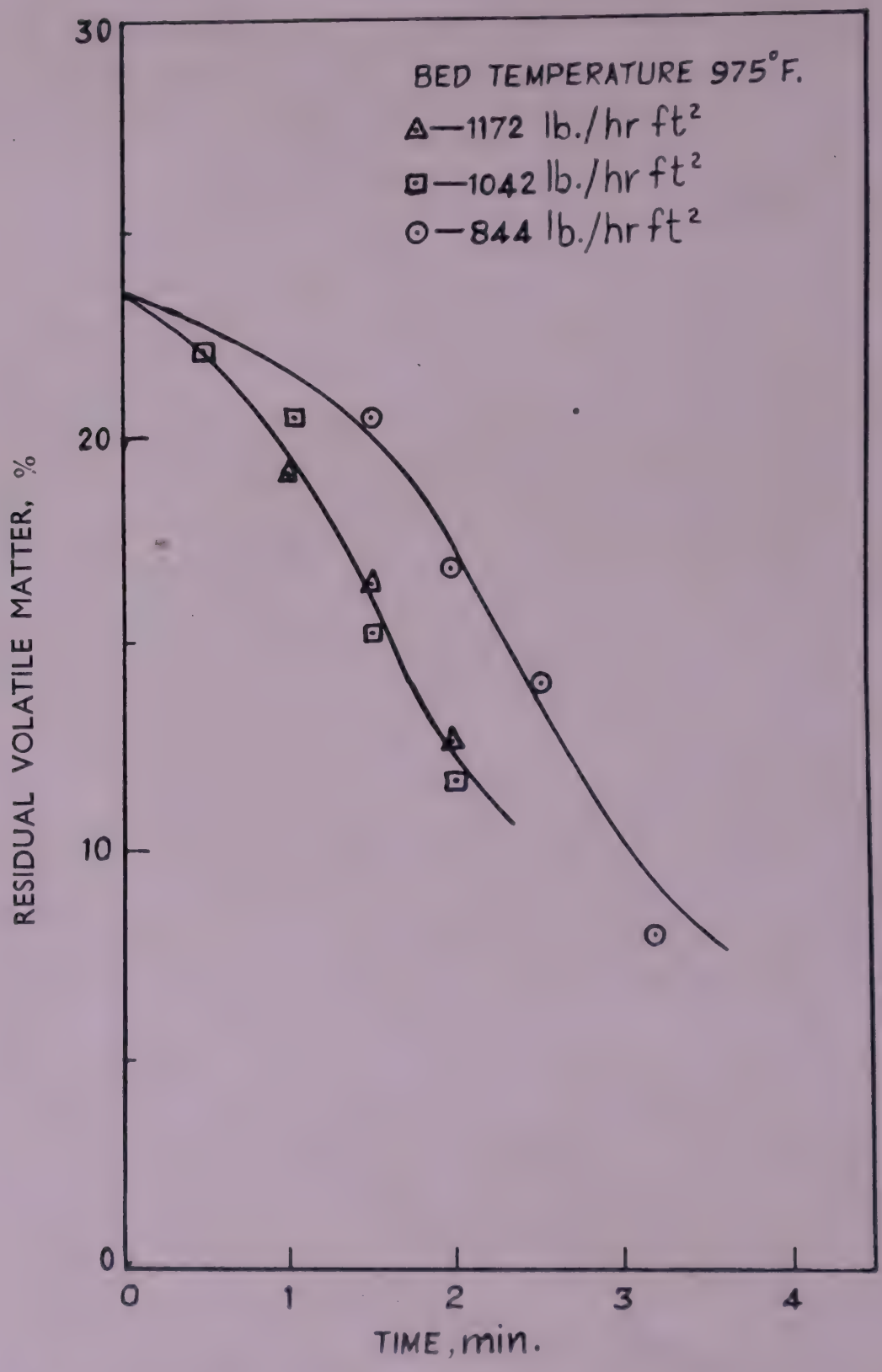


FIG. 4a—EFFECT OF MASS VELOCITY AND TIME OF RESIDENCE ON DECREASE IN VOLATILE MATTER

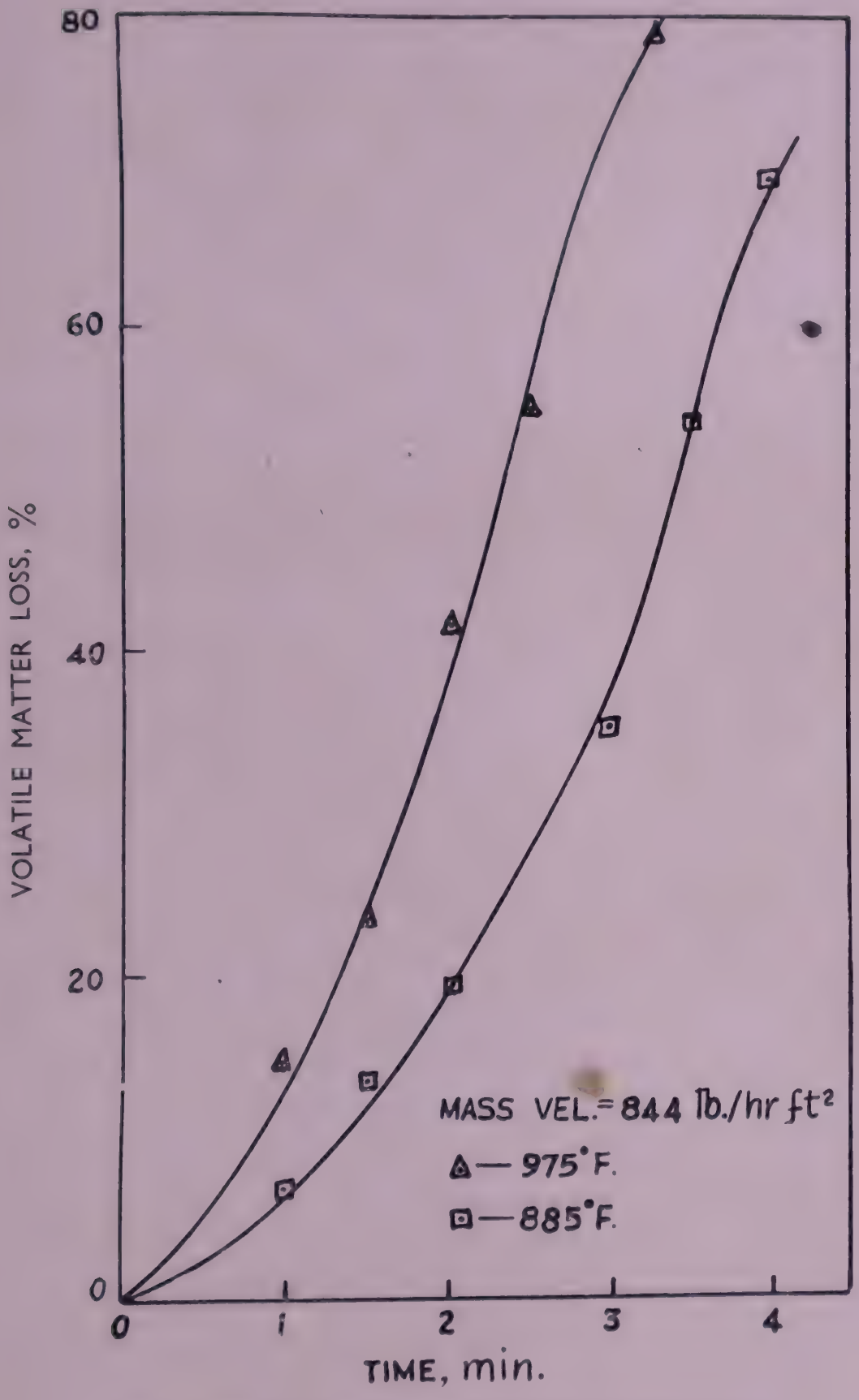


FIG. 5—EFFECT OF TEMPERATURE ON RATE OF DEGASIFICATION

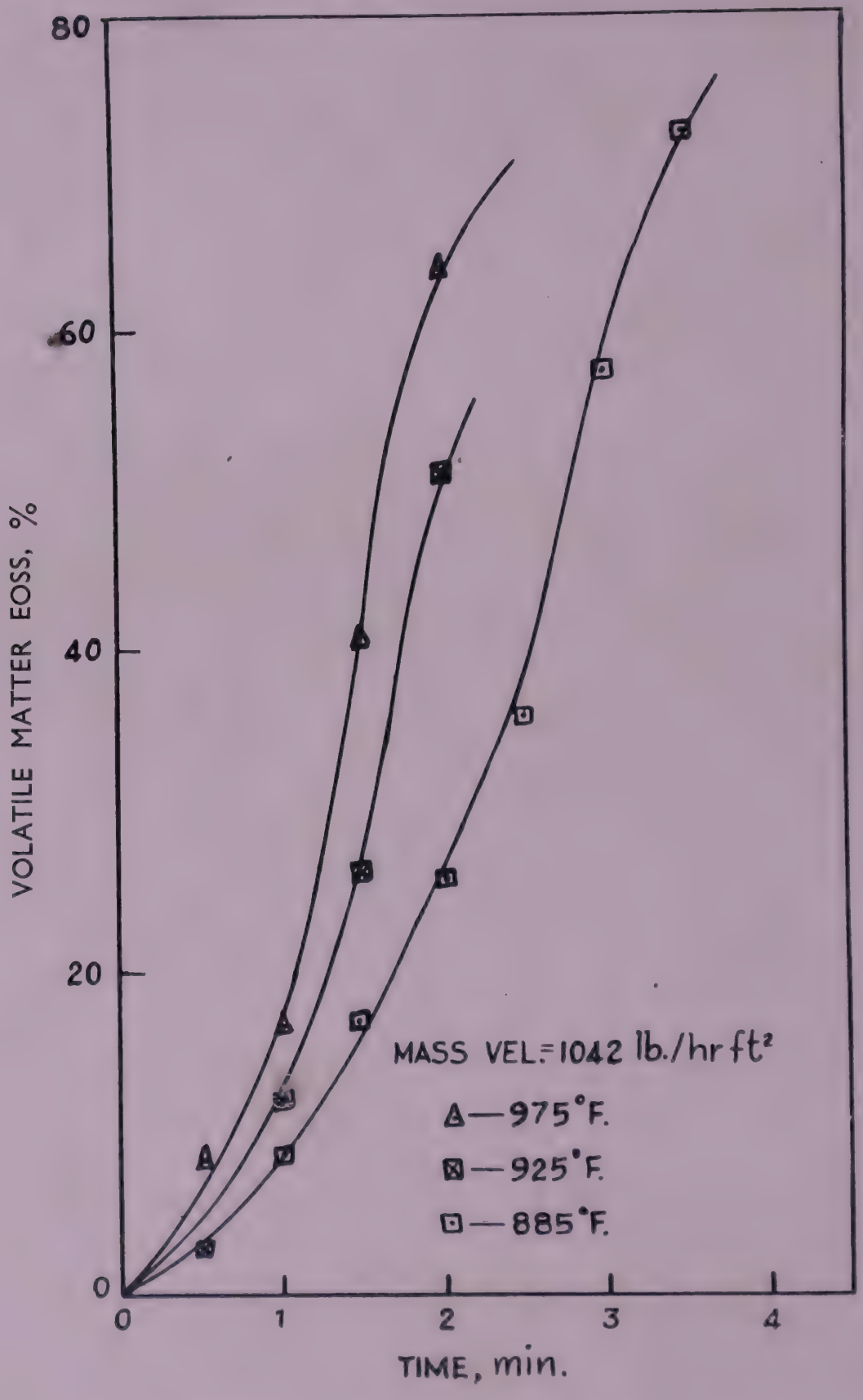


FIG. 5a—EFFECT OF TEMPERATURE ON RATE OF DEGASIFICATION

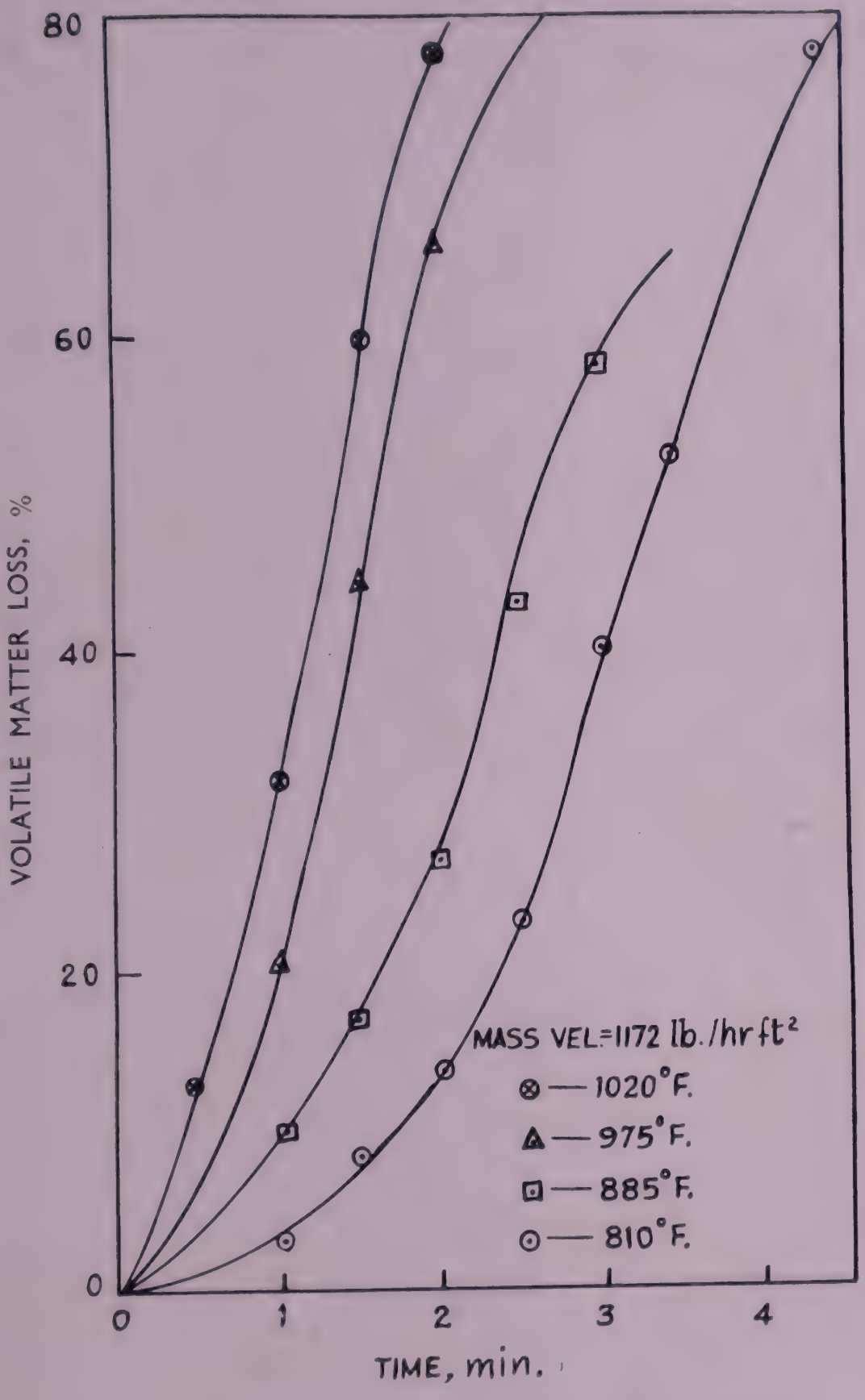


FIG. 5b—EFFECT OF TEMPERATURE ON RATE OF DEGASIFICATION

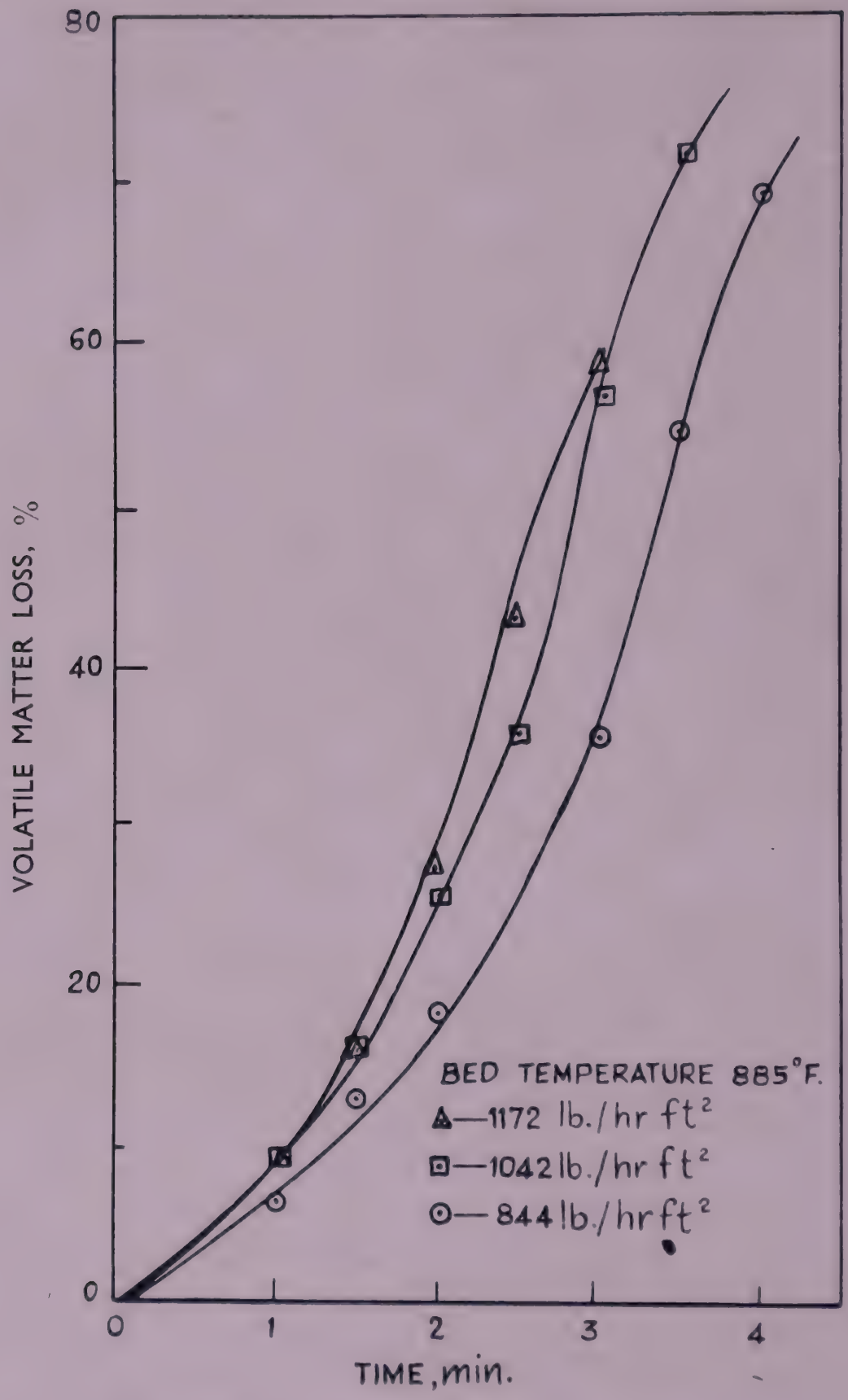


FIG. 6—EFFECT OF MASS VELOCITY ON RATE OF DEGASIFICATION

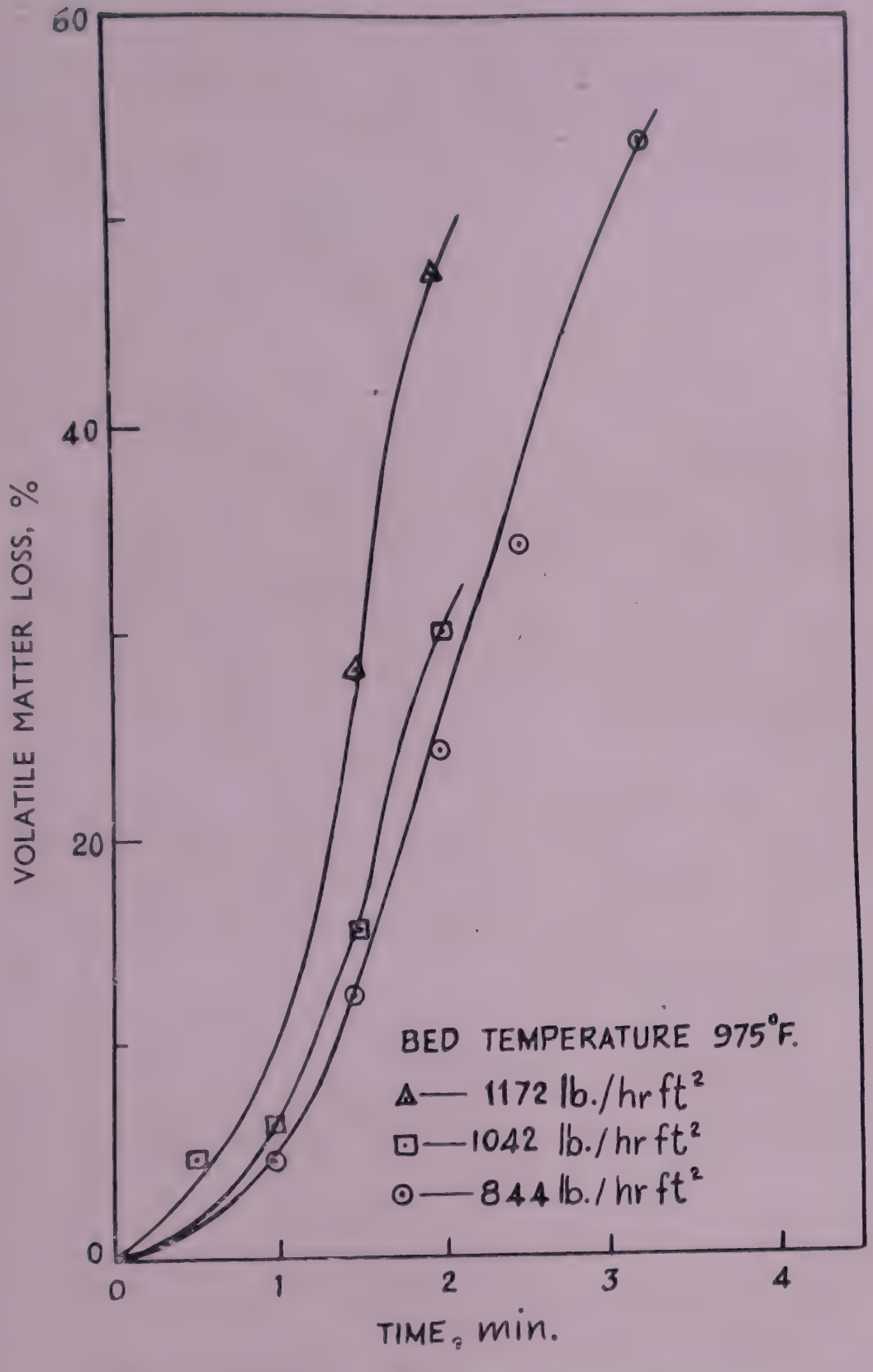


FIG. 6a—EFFECT OF MASS VELOCITY ON RATE OF DEGASIFICATION

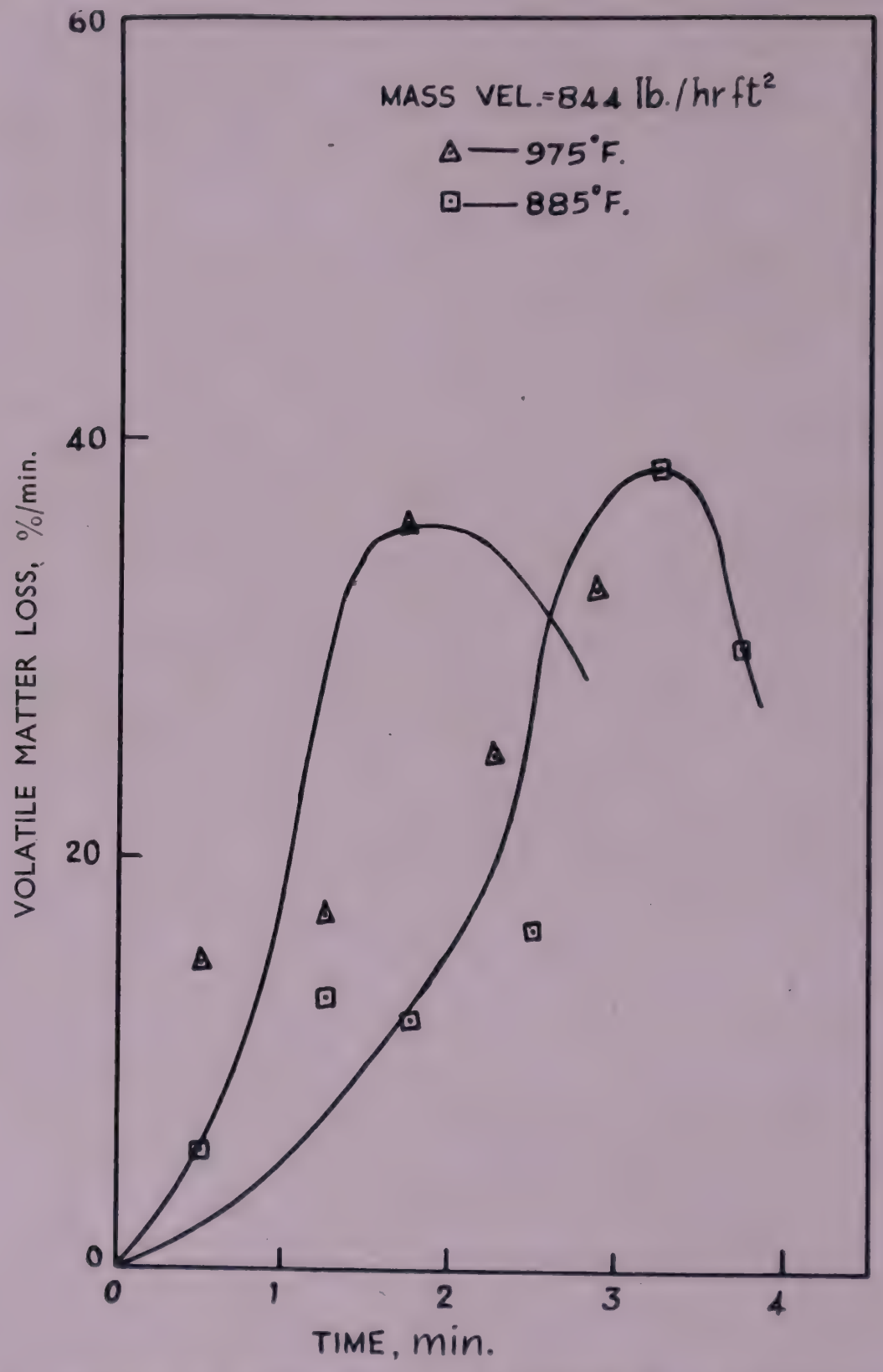


FIG. 7—EFFECT OF BED TEMPERATURE AND TIME OF RESIDENCE ON RATE OF DEGASIFICATION

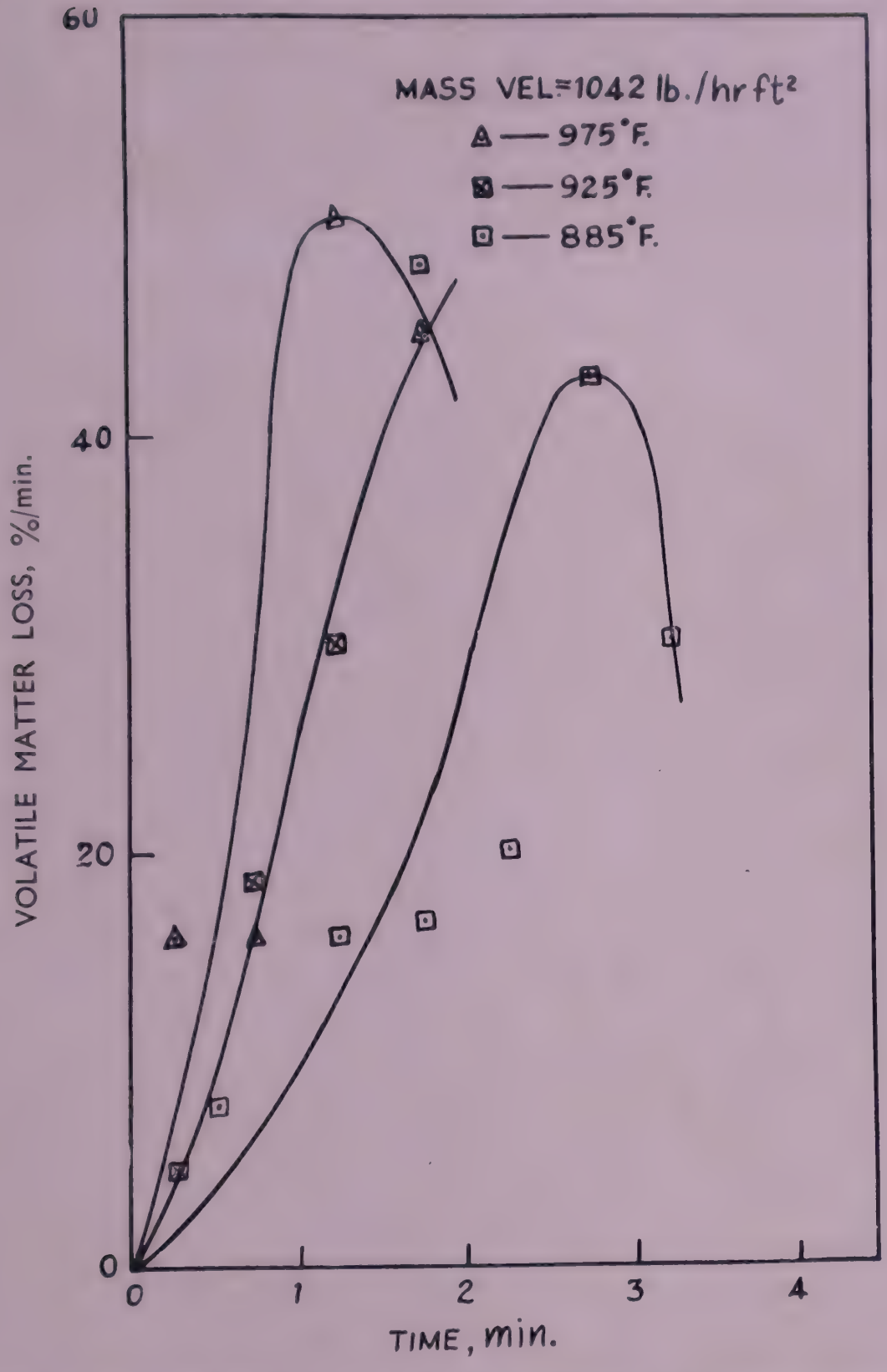


FIG. 7a—EFFECT OF BED TEMPERATURE AND TIME OF RESIDENCE ON RATE OF DEGASIFICATION

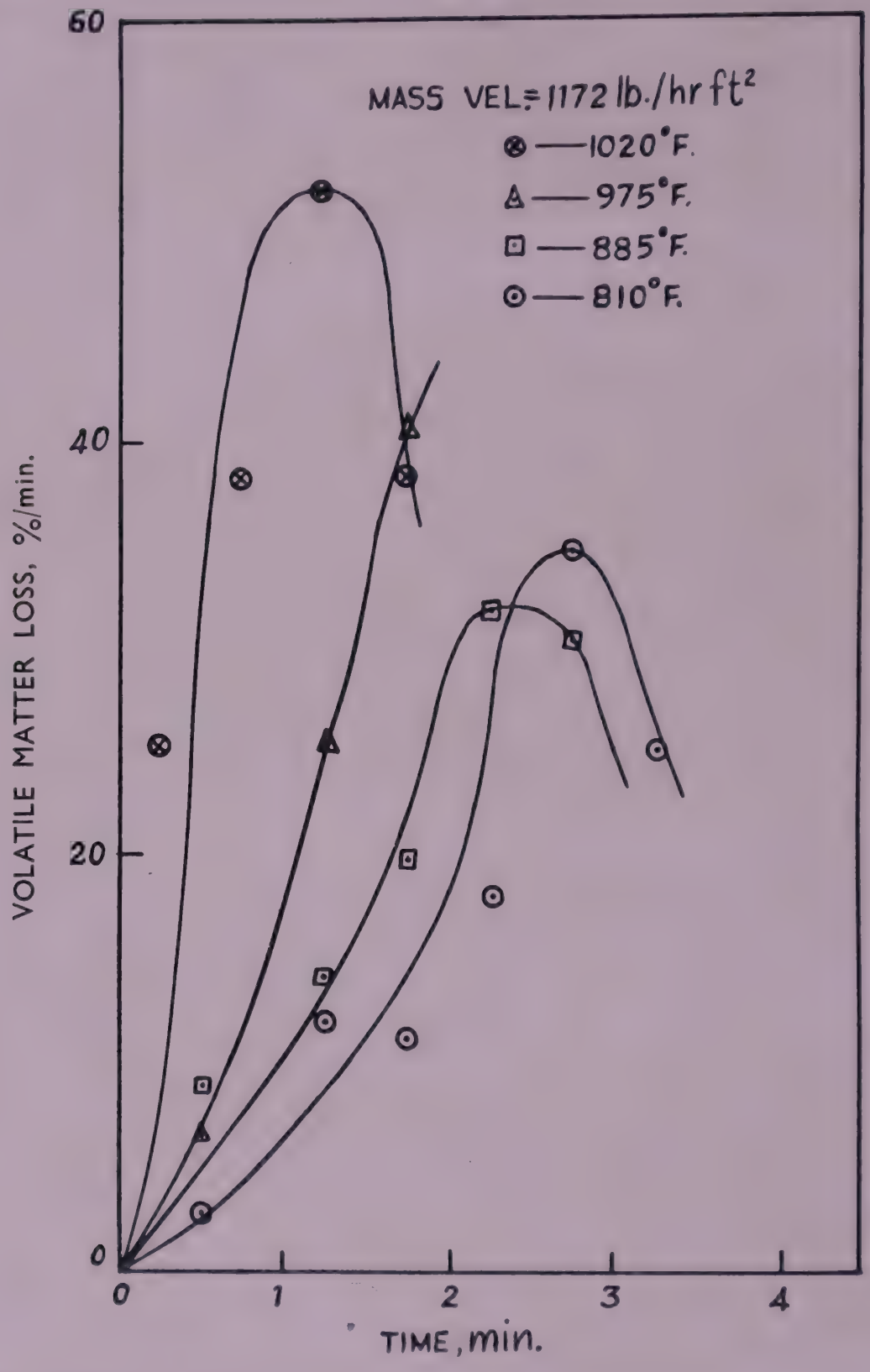


FIG. 7b—EFFECT OF BED TEMPERATURE AND TIME OF RESIDENCE ON RATE OF DEGASIFICATION

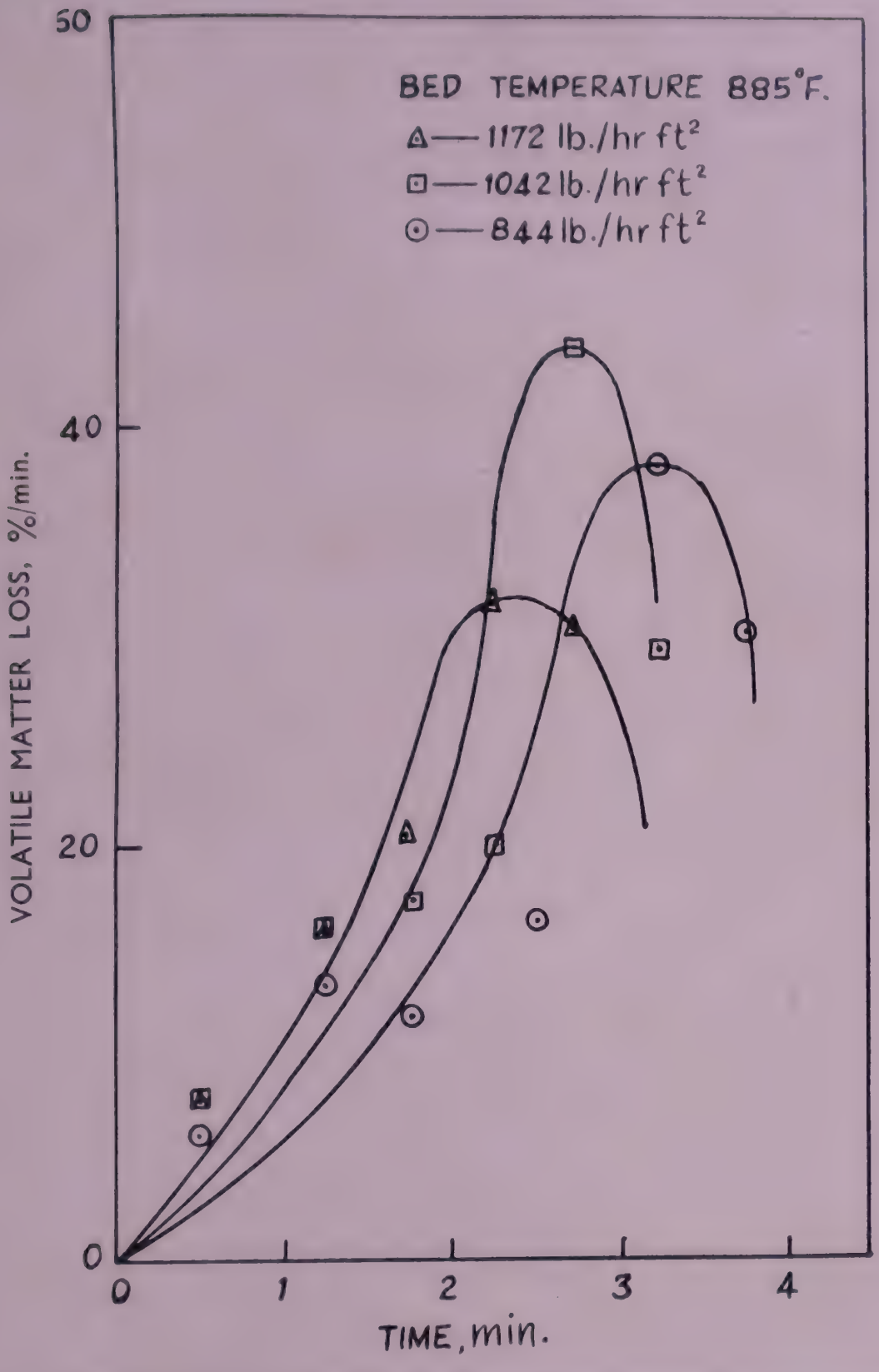


FIG. 8—EFFECT OF MASS VELOCITY AND TIME OF RESIDENCE ON RATE OF DEGASIFICATION

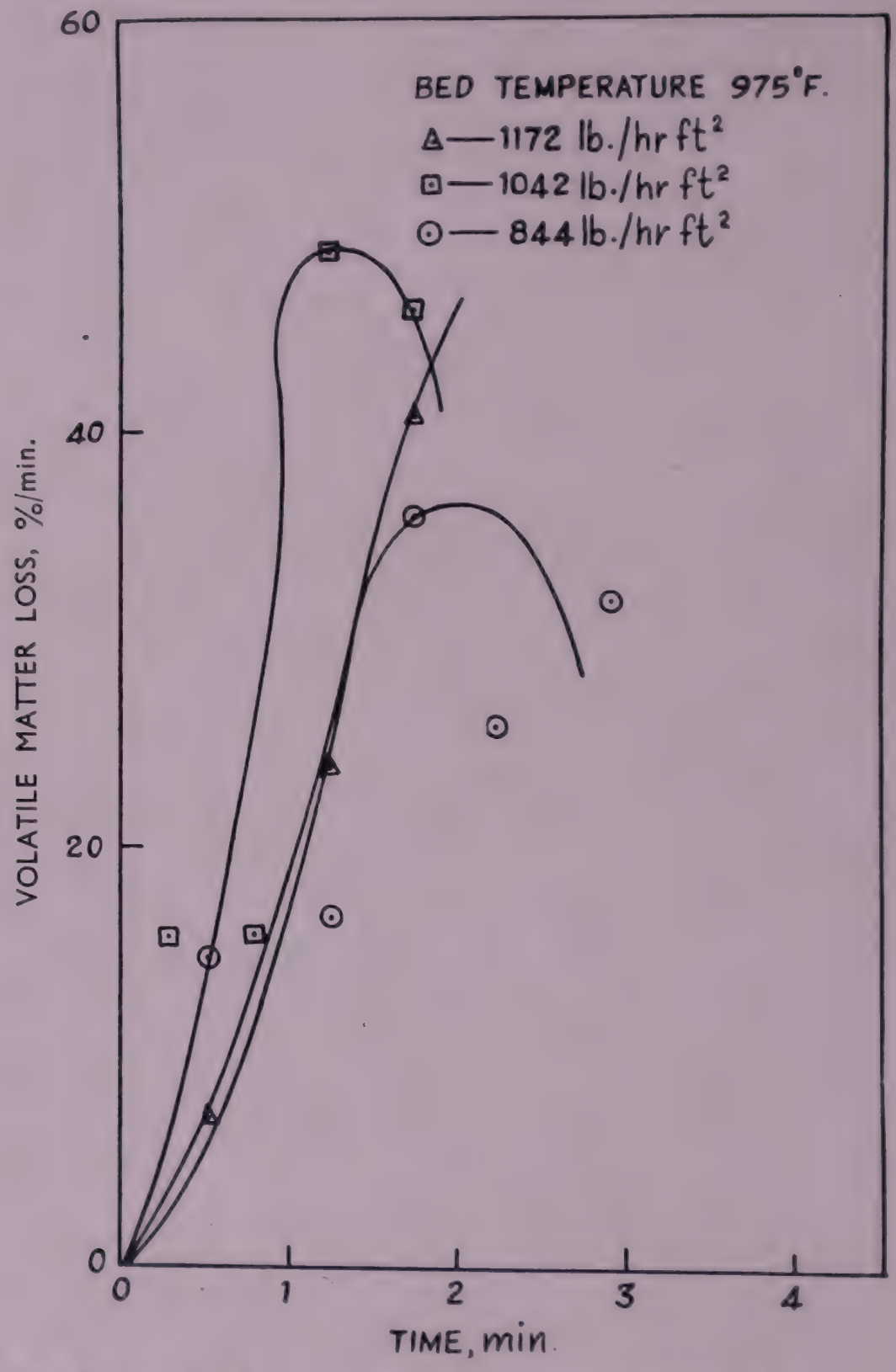


FIG. 8a—EFFECT OF MASS VELOCITY AND TIME OF RESIDENCE ON RATE OF DEGASIFICATION

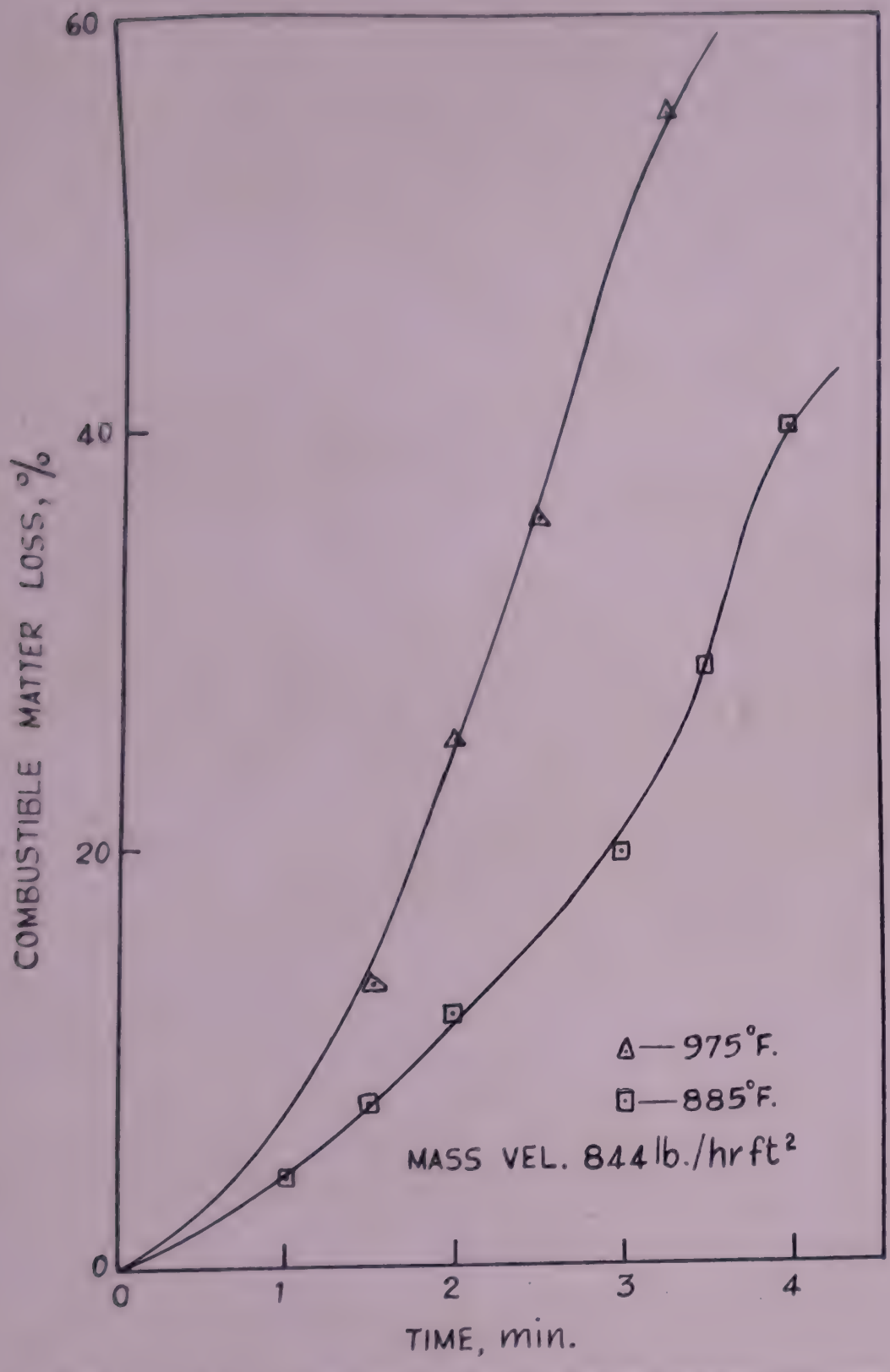


FIG. 9—EFFECT OF BED TEMPERATURE ON RATE OF LOSS OF COMBUSTIBLE MATTER

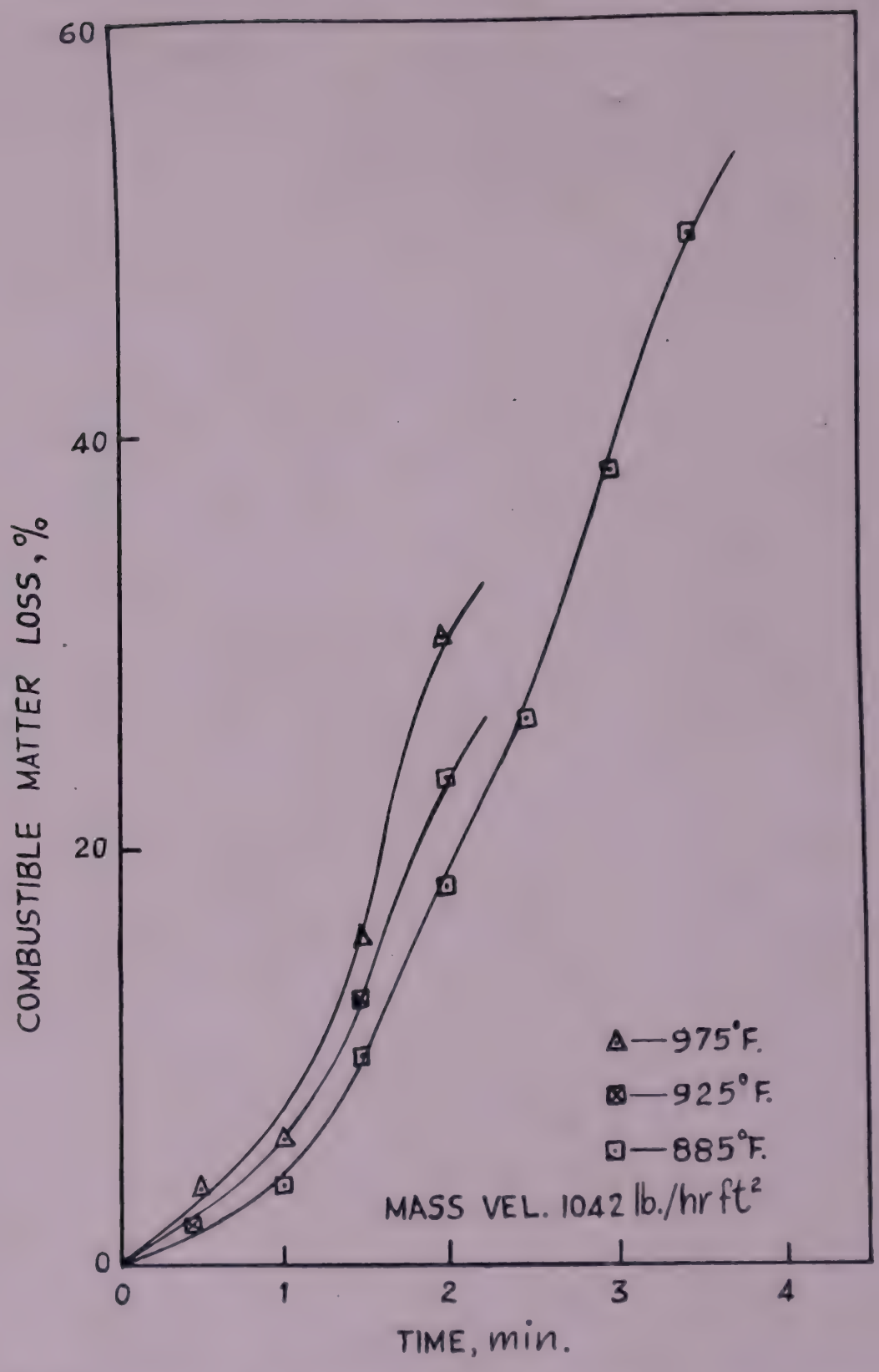


FIG. 9a—EFFECT OF BED TEMPERATURE ON RATE OF LOSS OF COMBUSTIBLE MATTER

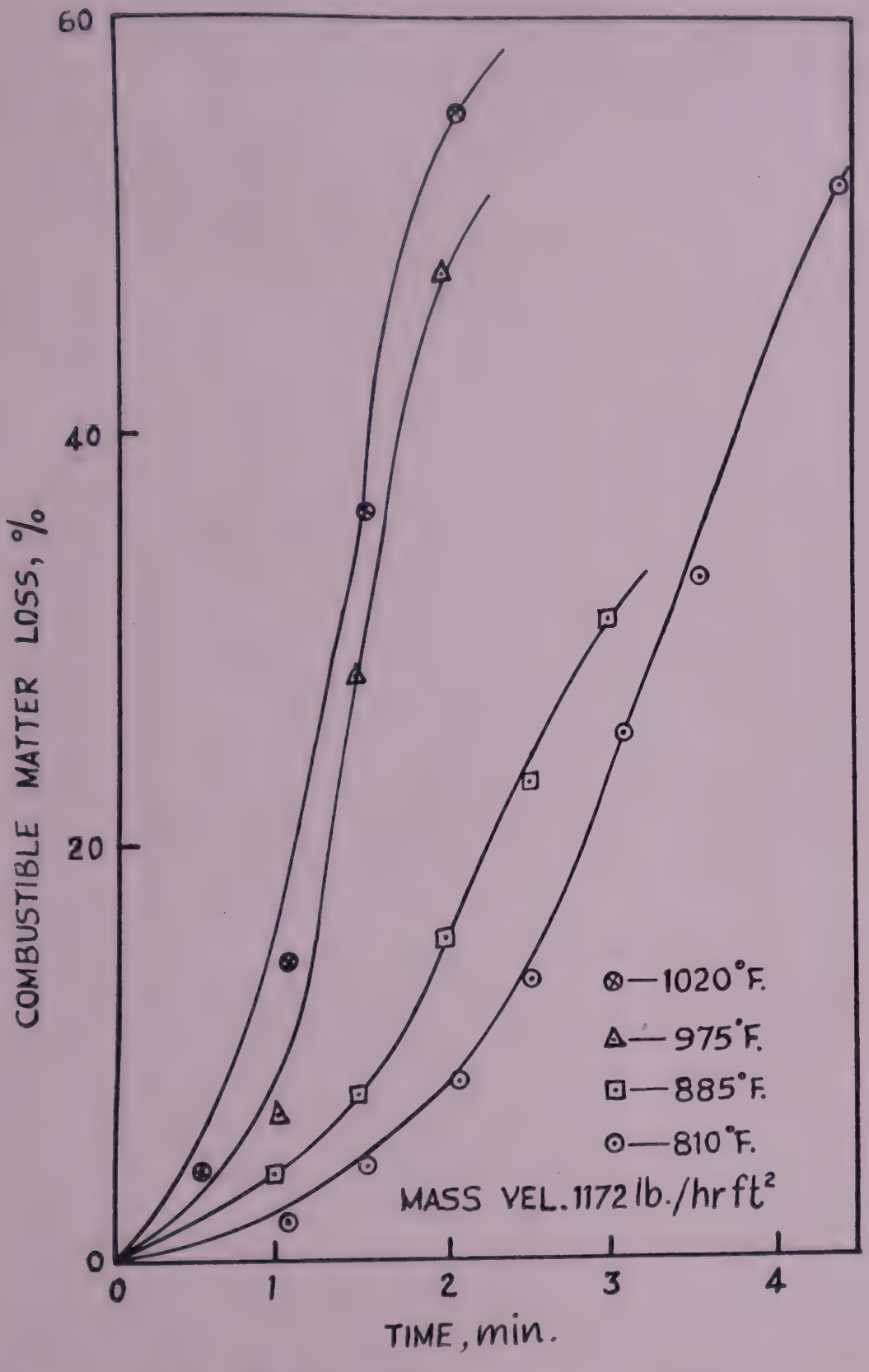


FIG. 9b—EFFECT OF BED TEMPERATURE ON RATE OF LOSS OF COMBUSTIBLE MATTER

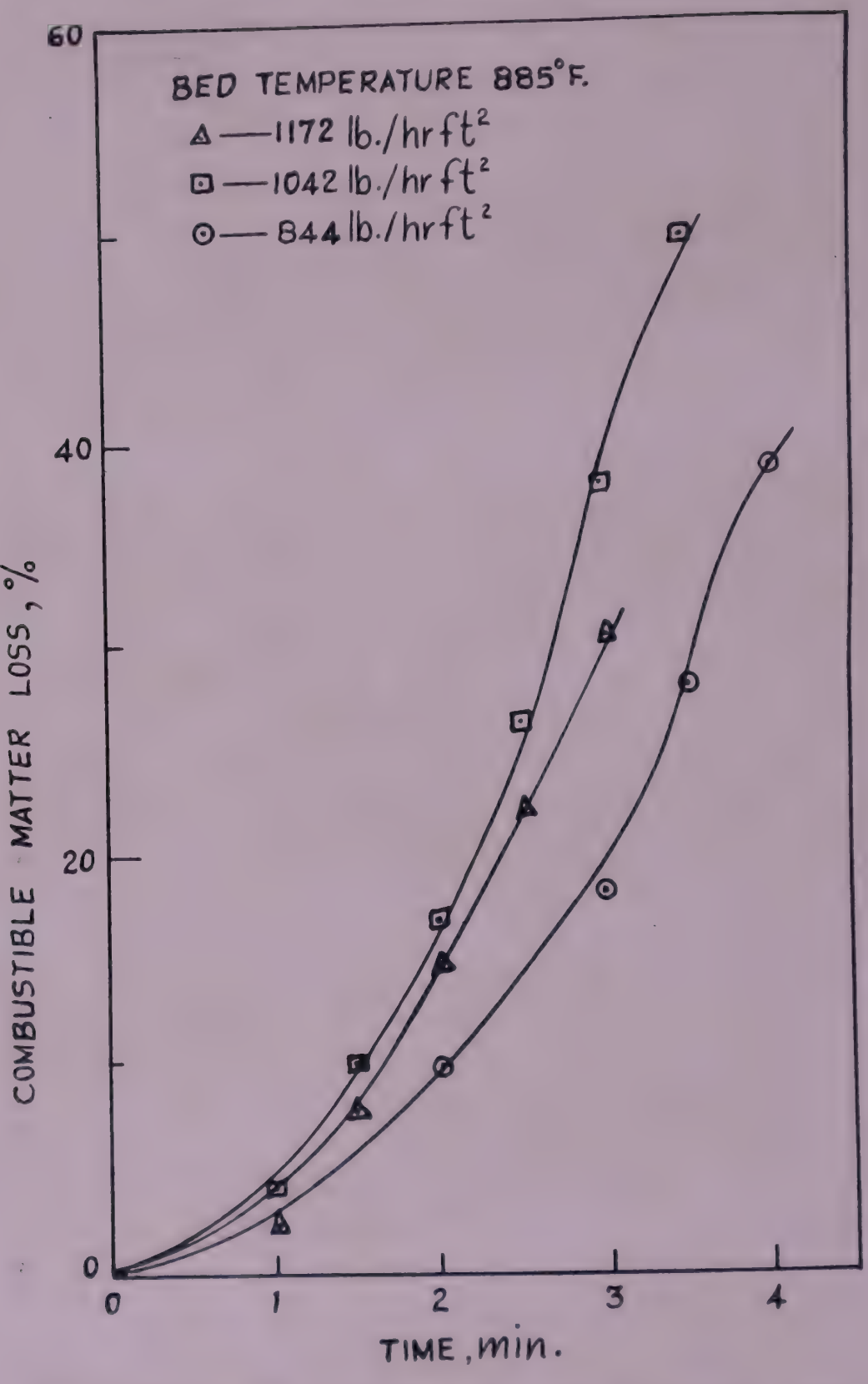


FIG. 10—EFFECT OF MASS VELOCITY ON RATE OF LOSS OF COMBUSTIBLE MATTER

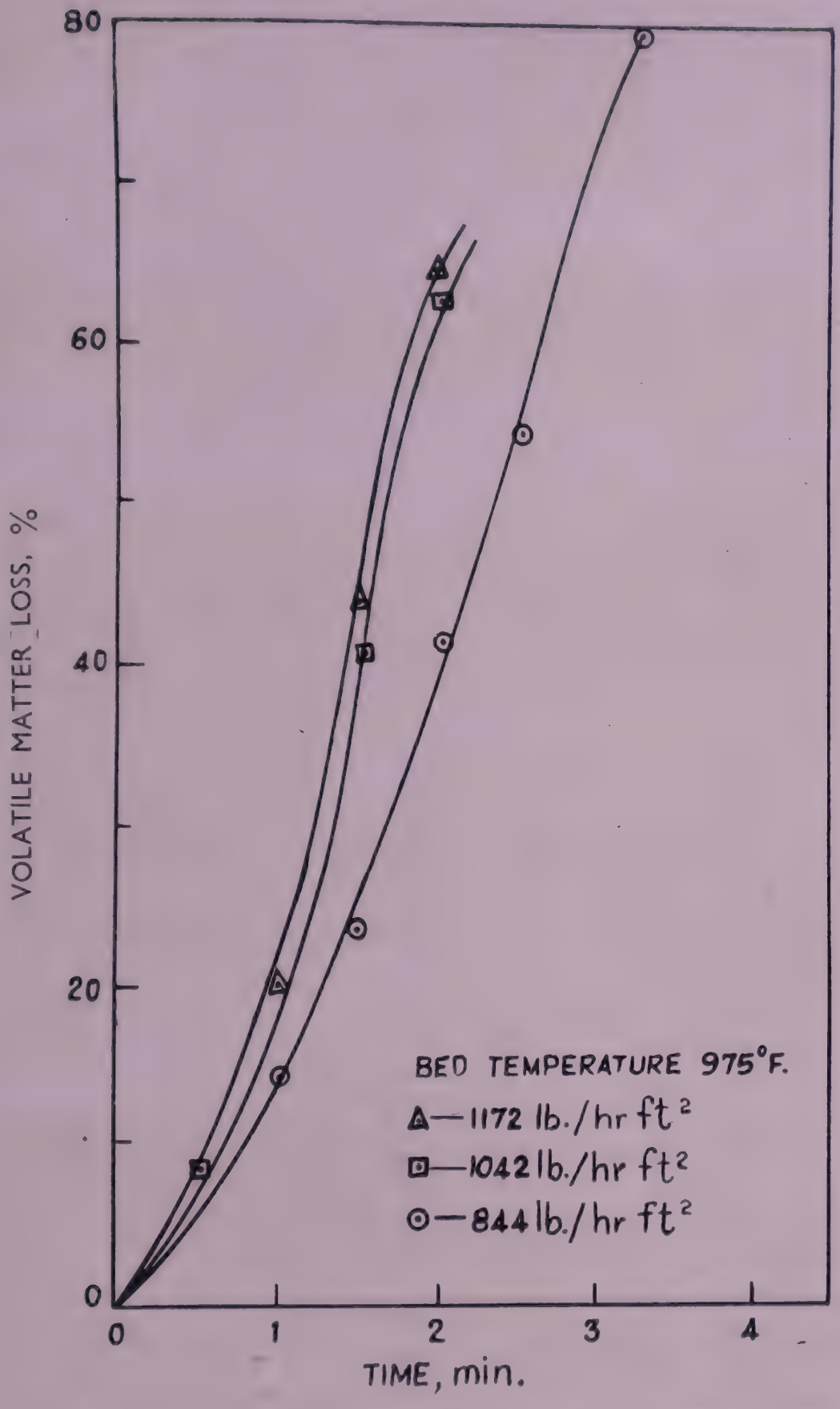


FIG. 10a—EFFECT OF MASS VELOCITY ON RATE OF LOSS OF COMBUSTIBLE MATTER

a coking coal is heated under inert atmosphere, the coking takes place in three stages, viz. (*i*) formation of metaplast, (*ii*) formation of semi-coke and gas from metaplast, and (*iii*) formation of coke from semi-coke. Of these, the first two take place in the temperature range of 350–550°C. It has been further shown by them that the reaction, coal → metaplast, is a first order reaction and follows the relation:

$$\frac{dP}{dt}=k_1P. \tag{1}$$

The second reaction, metaplast → semi-coke + gas, has also been shown by them to be a first order reaction and is given to be

$$\frac{dM}{dt}=k_1P-k_2M \tag{2}$$

$$\text{and, } G=P_0-P-M \tag{3}$$

where P_0=amount of coal (initial), P=amount of coal (at any time), M=amount of metaplast, G=amount of gas, k_1, k_2=reaction velocity constants and t=time.

According to Van Krevelen and Chermin[19], as the temperature of maximum plasticity and the temperature of maximum degassing are not much different in the case of heating of coking coal at constant rate, the value of the reaction constants k_1 and k_2 can be taken to be equal.

Accordingly, the following equations can be deduced:

$$G=P_0\,[1-(kt+1)e^{-kt}] \tag{4}$$

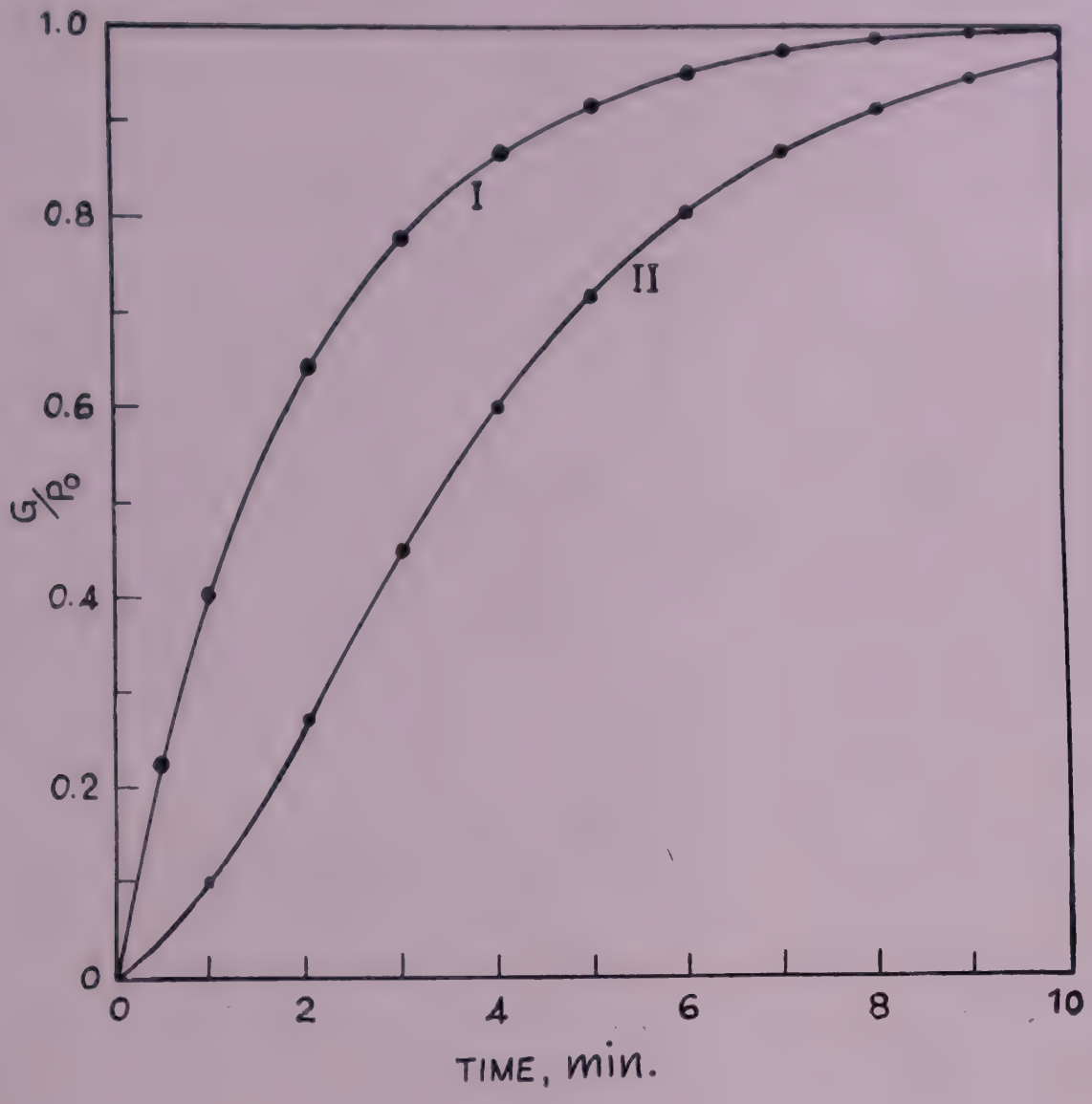
$$\text{or, } G/P_0=1-(kt+1)e^{-kt} \tag{5}$$

The one-stage degassification reaction can be written as:

$$G=P_0\,(1-e^{-kt}) \tag{6}$$

Rigorous application of this mechanism to the fluidized bed carbonization of non-coking coal is difficult. The essential difference is that the carbonization reactions have always been accompanied with oxidation reaction, and secondly, in the case of non-coking coal, the formation of definite plastic zone has not been established before the degassing reaction begins.

In Fig. 11, theoretical plots are shown for the degassification reaction based on single-stage and two-stage mechanisms and represented by Equations (5) and (6) respectively. Figs. 12 & 12a give the relation between the percentage of gas evolved during carbonization and time for present data. When this is compared with the theoretical plots (Fig. 11) it is observed that the experimental curve is similar in nature to the theoretical one represented by the two-stage process. Furthermore, some swelling of the coal particles was observed showing definitely that the plastic stage transformation takes place, and it is, therefore, thought probable that carbonization reaction in a fluidized bed is a two-stage process, the first stage being formation of a plastic mass though momentary, followed later by the degassing mechanism.



$$I\text{—}G/P_0 = (1 - e^{-kt})$$

$$k = 0.5 \frac{1}{\text{MIN.}}$$

$$II\text{—}G/P_0 \approx \left[1 - (kt + 1)\, e^{-kt}\right]$$

$$k = 0.5 \frac{1}{\text{MIN.}} \quad \text{(TAKEN ARBITRARILY)}$$

FIG. 11—THEORETICAL PLOT SHOWING RATE OF DEGASIFICATION

Based on the above considerations the average values of k for this reaction have been found out graphically for the present data. Using the values of k thus obtained, the theoretical values of G/P_0 have been recalculated for the same time and compared with the experimental values (Table 4). It can be seen from Figs. 13 & 13a that they agree within fair limits suggesting that the assumption of the process being governed by two-stage mechanism is valid.

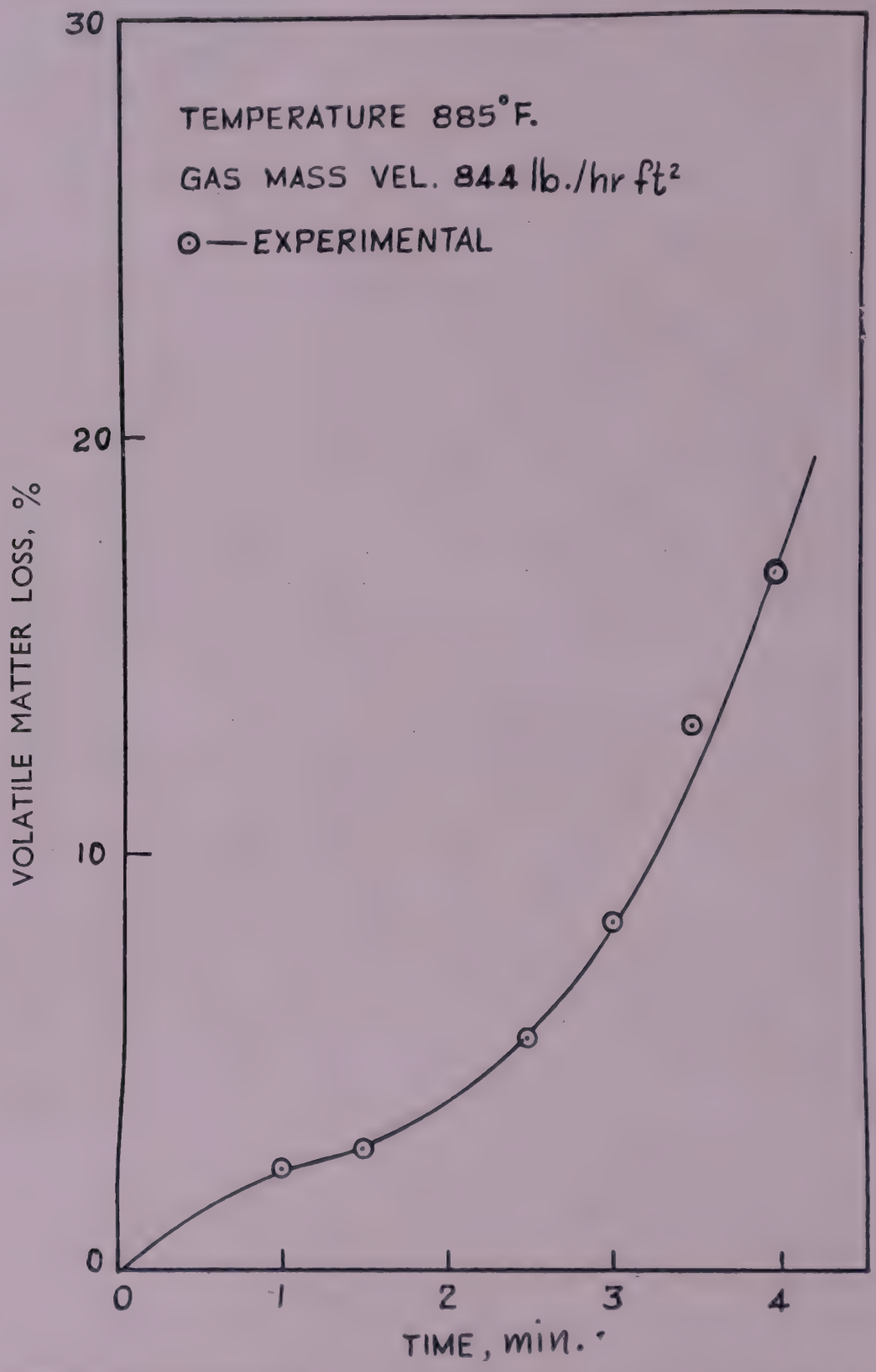


FIG. 12—EXPERIMENTAL PLOT SHOWING LOSS OF VOLATILE MATTER (per 100 g. of coal)

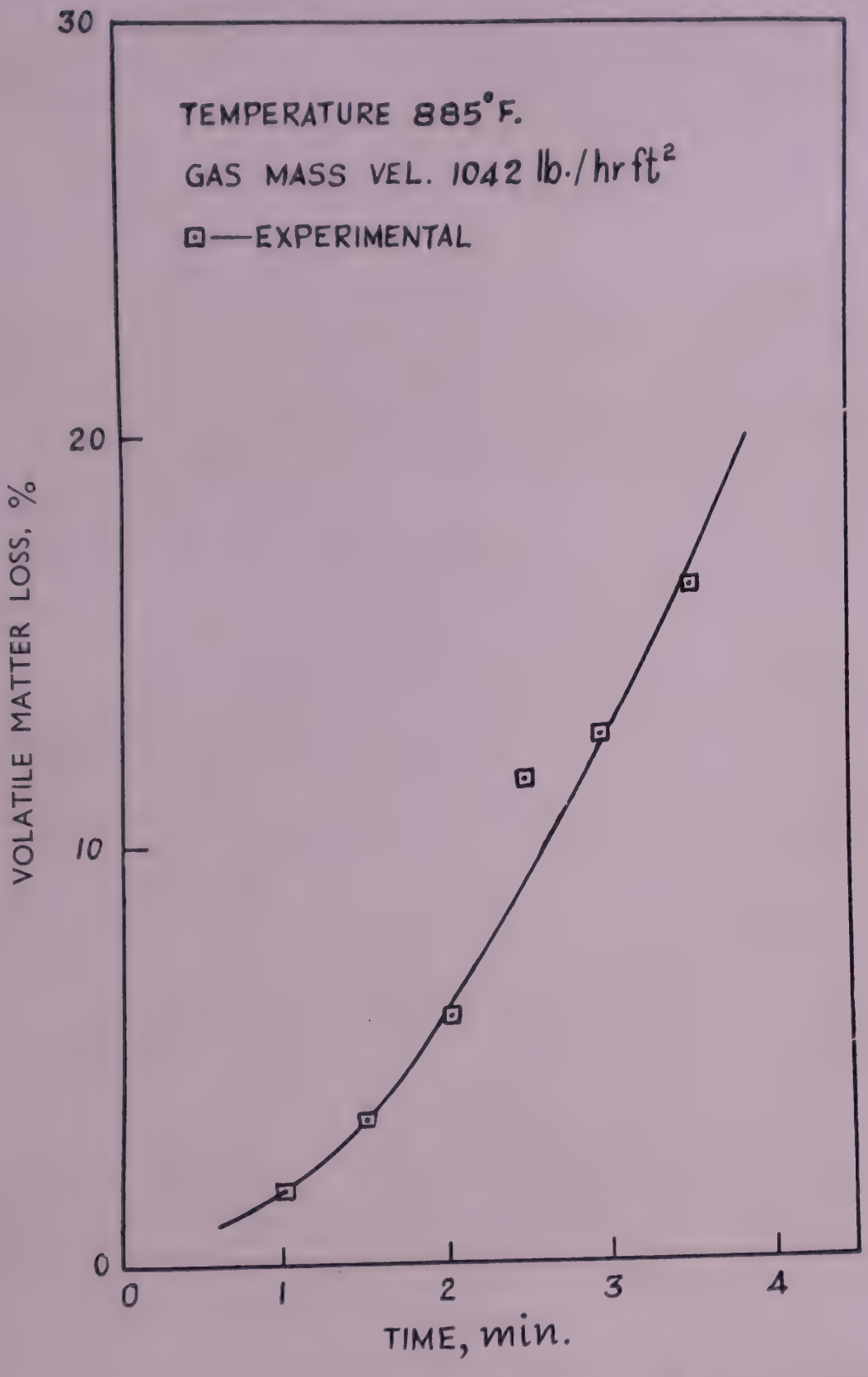


FIG. 12a—EXPERIMENTAL PLOT SHOWING LOSS OF VOLATILE MATTER (per 100 g. of coal)

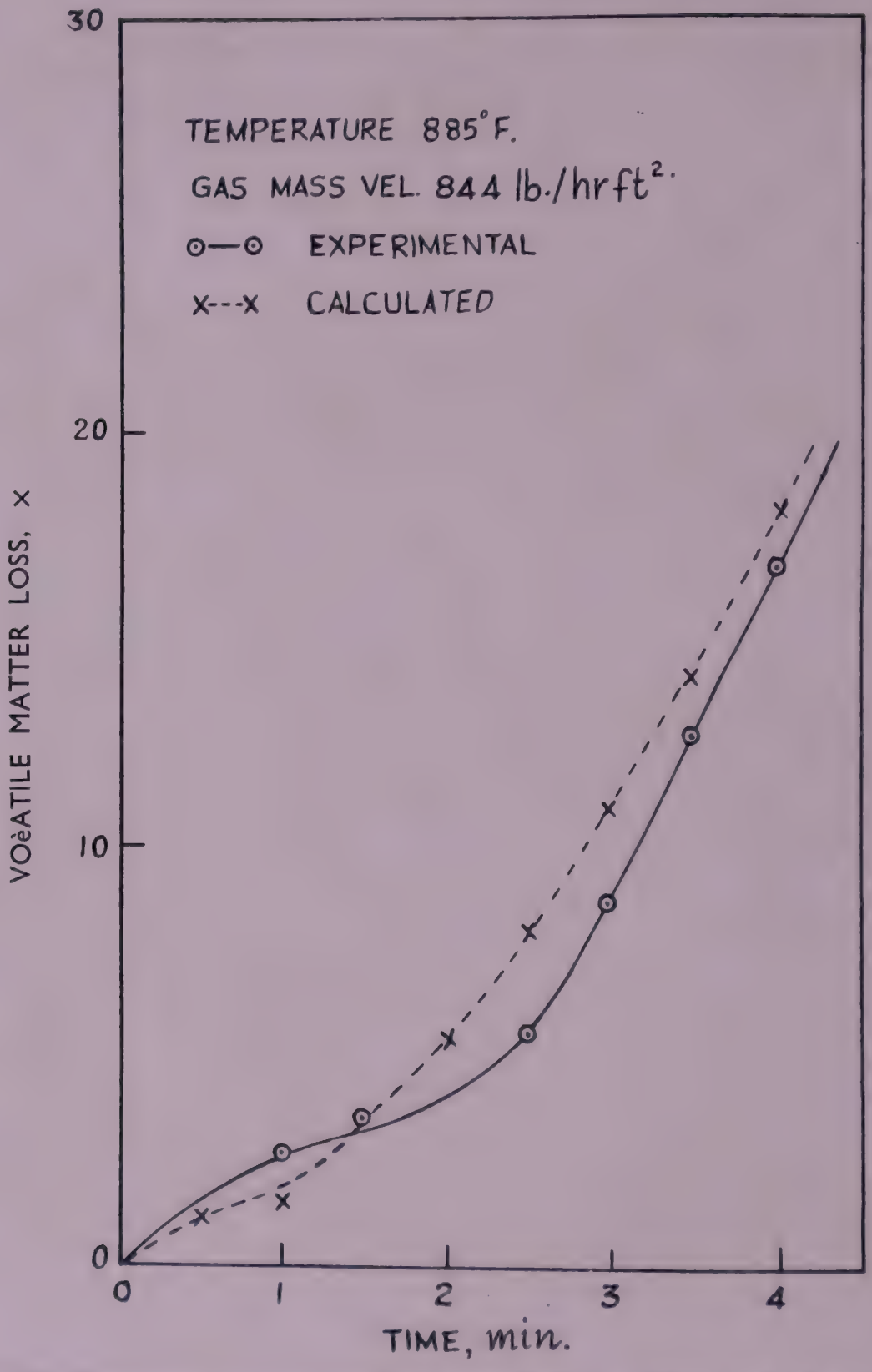


FIG. 13—COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF LOSS OF VOLATILE MATTER (per 100 g. of coal)

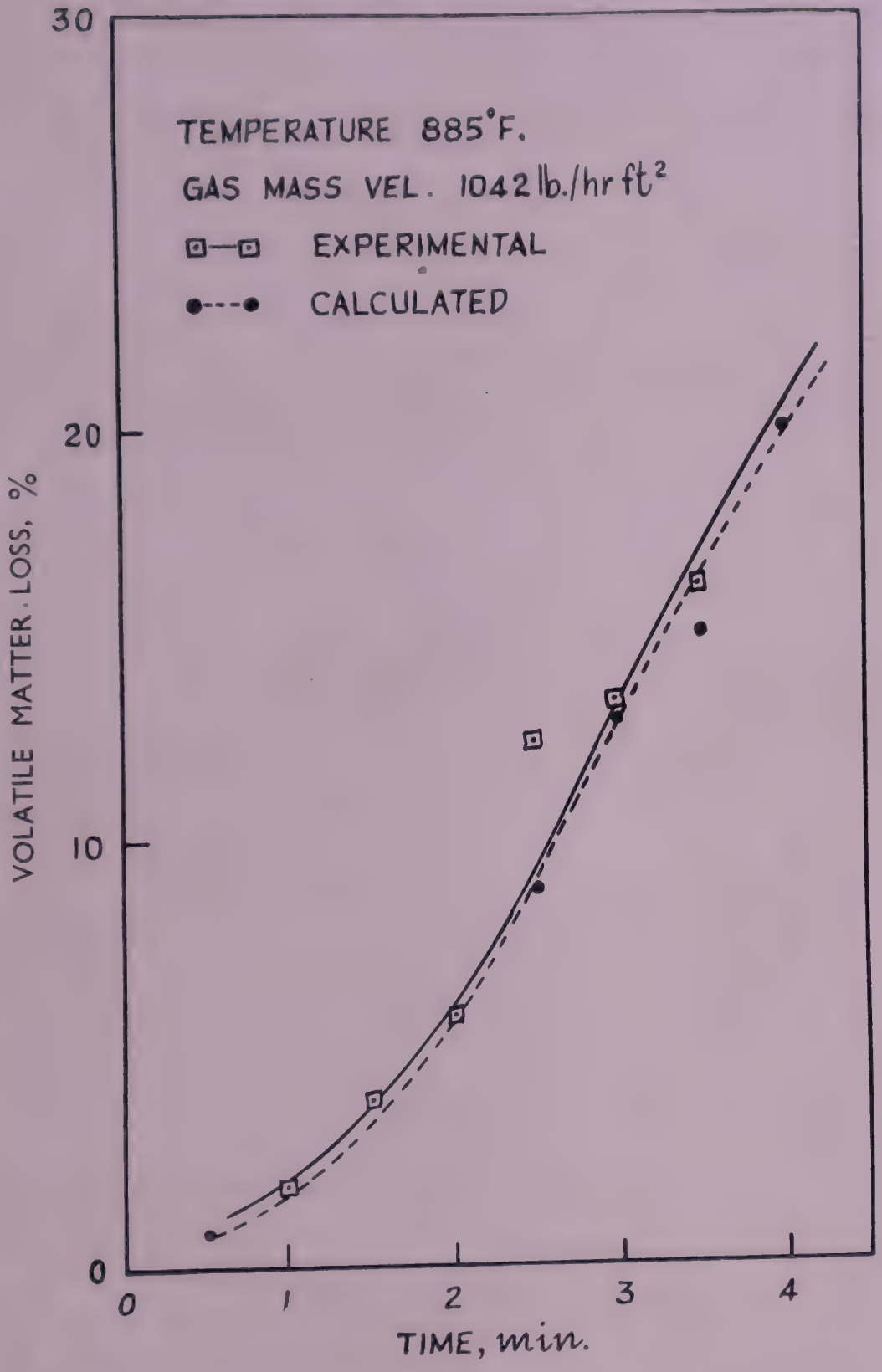


FIG. 13a—COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF LOSS OF VOLATILE MATTER (per 100 g. of coal)

TABLE 4—CALCULATED RESULTS SHOWING RATE OF DEGASIFICATION

t *min.*	kt	1+kt	e^{kt}	$(1+kt)e^{-kt}$	G/P_o
		(*Air mass velocity*, 844 *lb./hr/sq. ft; and* $K=0{\cdot}183$)			
0·5	0·0915	1·092	1·096	0·990	0·010
1·0	0·183	1·183	1·200	0·987	0·013
1·5	0·275	1·275	1·317	0·970	0·030
2·0	0·366	1·366	1·442	0·945	0·055
2·5	0·457	1·457	1·590	0·915	0·085
3·0	0·550	1·550	1·735	0·895	0·105
3·5	0·640	1·640	1·900	0·865	0·135
4·0	0·732	1·732	2·100	0·825	0·175
		(*Air mass velocity*, 1042 *lb./hr/sq. ft; and* $K=0{\cdot}200$)			
0·5	0·1	1·1	1·105	0·995	0·005
1·0	0·2	1·2	1·221	0·982	0·018
1·5	0·3	1·3	1·350	0·964	0·036
2·0	0·4	1·4	1·492	0·938	0·062
2·5	0·5	1·5	1·650	0·910	0·090
3·0	0·6	1·6	1·822	0·878	0·128
3·5	0·7	1·7	2·014	0·846	0·154
4·0	0·8	1·8	2·226	0·797	0·203

In view of the complicated nature of the reaction, it is only possible to arrive at an empirical relation regarding the reaction rate. Further work to corroborate the above mechanism of carbonization under fluidized bed conditions using both coking and non-coking coals under inert atmosphere is in progress.

Acknowledgement

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Plant for Manufacture of Potassium Chlorate

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Details of the plant designed and set up for the electrolytic production of potassium chlorate by direct electrolysis of potassium chloride are given.

A plant (capacity, 2 tons/day) for the production of potassium chlorate by direct electrolysis of potassium chloride solution has been designed and constructed at Mettur on the basis of data obtained through laboratory and pilot plant investigations. These are briefly described in this paper.

EXPERIMENTAL WORK

For collecting the data for designing the cells for the electrolysis, investigations were carried out using a cell of size 61 cm. × 61 cm. × 61 cm. and 15 blades of graphite of size 28 cm. × 15 cm. × 3 cm. as anodes and perforated mild steel plates as cathodes. The current in the cell was varied from 200 to 2000 amp. and the current efficiency and performance of the cell were evaluated. The data indicated that low current concentration and high anode current density in the cell give a satisfactory current efficiency.

Designing of Cell. The designing of a cell for operation at 6000 amp. was taken up. For this, the optimum and economic current concentration and current density had to be determined. A low current concentration would result in a cell of large size and hence high capital cost and large space. Yet a low current concentration of about 3 amp./litre was preferred in order to make sure of a high current efficiency. This is important particularly in a process where the energy consumption is high (6-7 kWh/kg.). As high current density results in increased voltage which offsets the advantage of increase in current efficiency, the anode current density was fixed between 6 and 7 amp./sq. dm. A cell was constructed and worked at 6000 amp. The cell (137 cm. × 137 cm. × 127 cm.) was made of 6 mm. mild steel plates. The top was covered with concrete slabs with suitable openings for anodes, thermometer and electrolyte feed and provided with a 2 cm. outlet.

Graphite plates of size 18·5 cm. × 3·2 cm. × 122 cm. were used as anodes. Twenty-four such anodes, in 4 rows of 6 each (two rows at either end) were suspended from the top of the cell by means of ebonite rods resting on the concrete slabs. The total anode area was 910 sq. dm. giving an anode current density of 6·6 amp./sq. dm. The anodes were connected to the main copper bus-bars by means of 24 mm. copper strands. The cathodes were made of 1 cm. thick mild steel wire netting of size 99 cm. × 137 cm. Three such nets were welded vertically to the sides of the tank. The anodes were suspended in the interspace between the cathode nets.

A 2 cm. standard pipe bent into a coil of 6 turns was fixed in the cell in between the two electrode assemblies to serve as a cooling coil.

The average current efficiency of the cell was 80 per cent. It was also observed that the hypochlorite in the electrolysed liquor got converted to chlorate after some time, as a result of which, 3 to 5 per cent increase in the current efficiency was obtained.

Accessory Equipment. After electrolysis is over, the process consists in crystallizing out the potassium chlorate from the cell liquor as crude crystals, recrystallizing to obtain pure crystals, drying and disintegrating the product. This part of the plant was designed from available data. The design incorporates the following features:

(1) An evaporative cooler for crystallizing out—this has been employed in place of the conventional crystallizers. It consists of a concrete tower, 152 cm. in diam. and 7·6 m. in height from the top of which the hot cell liquor is sprayed. From the bottom of the tower air is blown through. Here the liquor cools from 48 to 36°C.

(2) All the pumps standardized to one type and capacity—this helps in changeability and also reduces the need to stock spares of different types and capacities of pumps.

(3) PVC material of construction to avoid corrosion which otherwise would be severe with chlorate.

The imported components of the plant are only two continuous-type centrifuges and PVC materials.

Layout of Plant. The final layout was evolved with the help of a table-top model made to scale, avoiding unnecessary cross movements of materials so that a smooth flow of materials and a saving of pipe lines are ensured. The plant is in four sections: (*i*) d.c. equipment and electrical plant, (*ii*) cells, (*iii*) process house, and (*iv*) disintegrator house and packing. The gas scrubbing system and the cooling tower have been located outside the building.

Description of Process. The cells are fed continuously with a feed solution containing 35 to 40 g./litre potassium chlorate and 260 to 270 g./litre potassium chloride. The liquor coming out of the cells after electrolysis analyses to 55–60 g./litre potassium chlorate and 250–60 g./litre potassium chloride. This is pumped into a concrete tank, where it gets the necessary

FIG. 1—A VIEW OF THE PROCESS ROOM

retention time. The liquor is then cooled in the evaporative cooler and then the slurry coming out at the bottom is pumped to a settling tank. The underflow from this tank containing settled crystals is centrifuged and potassium chlorate of about 95 per cent purity is recovered. The clear overflow is recycled to the cell after dissolving potassium chloride.

The crude crystals are purified by recrystallization, and dried to obtain a product of 99·9 per cent purity. The product is then disintegrated and packed in 50 kg. wooden cases lined with waterproof paper.

The consumption of raw materials and utilities per ton of the product are: KCl, 700 kg.; HCl, 55 kg.; $K_2Cr_2O_7$, 9 kg.; graphite, 30 kg.; electrical energy, 7000 kWh; and steam (90 p.s.i.g.), 1300 kg.

Some Aspects of Fractionating Tray Design and Selection

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Various types of fractionating columns used commonly in industry are described. Their region of satisfactory operation for liquid and vapour flow and the overall column efficiency are discussed with particular reference to the design of bubble cap trays. The capacities and costs of various types of trays are compared.

Fractionating towers are designed on the basis of three considerations: (*i*) number of theoretical stages for a given separation, (*ii*) tower diameter, and (*iii*) type and layout of the fractionating tray.

The actual number of trays required depends on the efficiency of separation which itself is a function of the tray design. Inasmuch as the initial investment in fractionating columns alone in typical petroleum plants amounts to about 10–15 per cent of the total investment, considerable work has been done and is being done to improve the design of fractionating trays with a view to keeping this investment to a minimum. A number of new designs have been evolved in recent years for improving the performance and reducing the cost.

The performance of the new trays is almost always compared with the older, more popular type, namely, the bubble cap tray. The point of comparison is the capacity and efficiency for a particular feed type and separation. From the point of view of cost, the investment required for a particular tray design may be low but the economic penalties due to poor performance may be so high as to make it unattractive in the long run. Thus no tray can be classified 'best' for all types of separations encountered in industry.

The primary aim of an efficient design is to be able to effect the given separation and to do it economically. The final choice of any one type of tray will depend on: (*i*) the initial investment, (*ii*) flexibility of operation and ease of control, and (*iii*) ease and economy of maintenance.

The present paper reviews briefly the more common types of vapour-liquid contacting devices and the qualitative region of satisfactory operation as determined by the various objectionable phenomena occurring in the contacting process. Certain design factors used in the design of bubble cap trays and a comparison of capacities and cost of the various types of trays are discussed.

TYPES OF FRACTIONATING COLUMNS

The common types of trays in use today are described below:

Bubble Cap Tray. This tray has been the most popular device used widely in chemical and petroleum industries. A large volume of published data exists on the performance of this type of tray. The chief merit of a well-designed bubble cap tray is its ability to maintain satisfactory efficiencies over wide ranges of liquid and vapour loads (Fig. 1a).

Sieve Tray. This type has not been as popular as the bubble cap type because of the comparative lack of performance data. It was believed that this type of tray had a narrow operating range. However, recent studies have shown that the range is quite high[1] and because of its larger capacity, higher efficiency and low initial as well as maintenance costs as compared to bubble cap trays, more attention is now being given to this type of tray (Fig. 1b).

Uniflux Tray. This can be considered as an improved version of bubble cap trays. The fundamental unit in a uniflux tray is an S-member with slots cut on one edge, the downstream edge. The vapours issuing from the slots boost the liquid across the tray. The ultimate capacity of a bubble cap tray is more often limited by downflow capacity than by any other cause. Efficiency also suffers in towers with high liquid downflow, probably because of excessive hydraulic gradient and resultant unequal slot submergence. The flow in this type of tray compensates for the liquid gradient under all conditions of flow and the dynamic slot submergence is thus uniform across the tray (Fig. 1c).

Flexi Tray. It is a valve-type tray with liftable valves of about 2 in. diam. retained by four-posted, plate-stamped spiders attached to the deck on a triangular pitch of 3–6 in. Alternate rows of valves (or caps) have different weights. The lighter caps open during the first 20–30 per cent of tray loading. The heavier caps open from this range up to 50–70 per cent of capacity. At higher rates all caps remain thrust open. Maldistribution of vapours due to the liquid gradient is thus reduced. It combines a capacity approaching that of a well-designed sieve tray with an efficiency and flexibility approaching those of a bubble cap tray (Fig. 1d).

Float Valve Tray. The valves of this tray consist of an angle, one side (the light edge) of which rests on rectangular slots (vapour risers) cut on the tray. The valves are retained by end brackets in a manner which restricts their vertical and horizontal movements. As vapour passes up the tray, it first pushes up the light edge which pivots at the heavy edge. At high vapour rates, the heavier edge is pushed upwards pivoting at the light edge. At about 20 per cent of the vapour design rate, irrespective of the liquid loading, all the valves are in operation with their light edges open. The edges usually face into the liquid flow. At about 40 per cent of design loading, the heavy edges start to rise until at 70 per cent when all the valves are in

FIG. 1—TYPES OF FRACTIONATING TRAYS

[*a*, BUBBLE CAP; *b*, SIEVE TRAY; *c*, UNIFLUX; *d*, FLEXITRAY; *e*, FLOAT VALVE; *f*, TURBOGRID; *g*, RIPPLE TRAY]

fully open position. Beyond this point, full loading is reached by increased pressure drop through the valves in full open position (Fig. 1e).

Turbogrid Tray. This tray consists of a grid of slots extending over the entire cross-section of the tray. The slots may be stamped or formed by two adjacent horizontal bars. This type of tray has no downcomer and the

liquid level is maintained by the dynamic balance of the liquid and vapour flows. A high capacity tray, it has found considerable application in industry (Fig. 1f).

Ripple Tray. This tray consists of a perforated plate formed into a sinusoidal wave pattern extending over the entire cross-section of the tower. The plates are oriented at 90° to aid in better liquid distribution. It has no downcomer and the liquid level is maintained by the dynamic balance of liquid and vapour flow rates (Fig. 1g).

Other types of trays are the Kaskade and Benturi with directional vapour flow which aid in reducing the liquid gradient across the tray. The Benturi type offers very low pressure drops, important in vacuum tower operation.

Region of Satisfactory Operation. The capacity of a fractionating tray is limited by its ability to handle efficiently the liquid and vapour loads for a given diameter of the column. The liquid and vapour loads may fluctuate widely over the design rates and the ability of the tray to bring about the contact between the fluids with a fair degree of efficiency determines the flexibility of a tray design.

For each type of tray design there exists a region of satisfactory operation beyond which some of the commonly occurring objectionable phenomena become prominent and render its operation as a contacting device inefficient and unsatisfactory. The qualitative region of satisfactory operation limited by the objectionable phenomena is shown in Fig. 2. The construction of quantitative diagrams is usually reported in literature in the case of bubble cap trays. However, the basic limitations imposed by such phenomena may be applied to other types of trays as well to determine their operating range.

The limits of satisfactory operation are determined by a number of factors which depend on the properties and flow rates of the fluids. Some of the factors and the design rules commonly used in sizing bubble cap trays will be considered.

Design of Bubble Cap Tray

Before fixing the bubble cap tray layout design, the tower diameter, tray spacing and cap design are usually fixed.

The tower diameter is normally determined from a consideration of Stoke's law which in effect considers that entrainment is the limiting factor. Tower diameters based solely on vapour load will usually be sufficient to handle the liquid load also. However, this is to be checked in the initial stages. This is important in the case of large-diameter towers, since the area is proportional to the square of the diameter, whereas the weir length varies as the diameter. There will be less weir possible per square foot of deck area as the diameter becomes larger.

The amount of liquid carried upward from one plate to another by

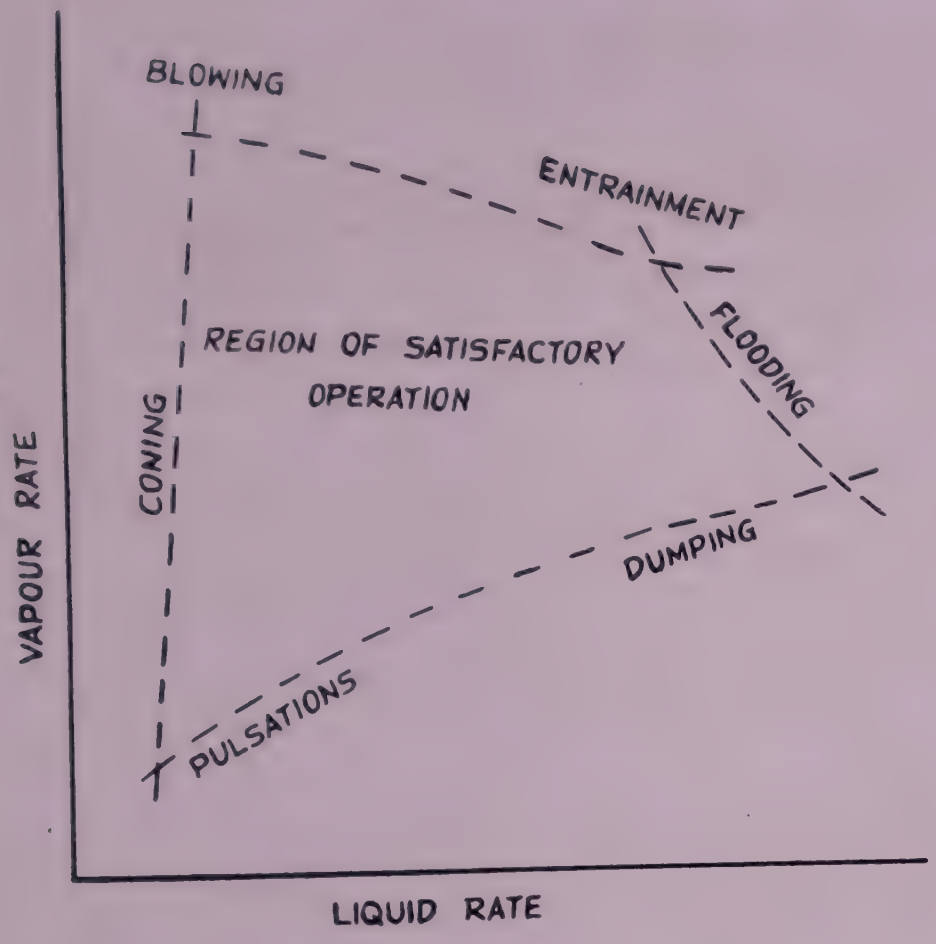

FIG. 2—REGION OF SATISFACTORY OPERATION (FOR EACH TYPE OF TRAY) LIMITED BY OBJECTIONABLE PHENOMENA

entrainment depends not only on the mass velocity but also on the plate spacing. There are numerous references to the effect of entrainment on tray efficiency. But there is no clear-cut limit, applicable to all cases, where entrainment causes difficulty. Only in some cases a large amount of entrainment could be permitted. Based on the experience in petroleum refining, the minimum tray spacing is set at 18 in. below which entrainment increases rapidly. One very practical consideration of plate spacing is concerned with having enough clearance between bubble decks to facilitate inspection and maintenance of trays. This requires a minimum of about 24 in. which leaves about 18 in. for movement.

Cap design is usually based on the practice followed by the company. Almost all the bubble caps used today are round with the riser, reversal and annular areas nearly equal and the slot area equal or larger. Cap diameters vary between 3 and 6 in. Economic considerations dictate 3 in. caps for $2\frac{1}{2}$–4 ft diam. columns, 4 in. caps for 4–8 ft columns and 6 in. for larger diameters. Caps are spaced on equilateral triangular pitch with pitch of $1\frac{1}{3}$–$1\frac{2}{3}$ times the cap diameter.

Weir length and height, downcomer size and clearance and the hydraulic gradient across the tray depend on the liquid flow rates. Slot opening, wet-cap pressure drop and vapour distribution are determined by vapour flow rates.

Weir Length and Height. The liquid flowing on to a plate must have its level regulated by an outlet weir, so that the caps always have a minimum submergence. The liquid will build up to a certain depth above the crest of the weir depending on the flow rate over the weir. For straight weirs, this is usually computed by the Francis weir formula:

$$Q = 179{\cdot}8\, Lh^{\frac{3}{2}}$$

where Q = U.S. gal./hr;
L = weir length, in.; and
h = height of liquid over weir, in.

Actually, this formula applies to continuous liquid phase while the fluid passing over the weir is a frothy mixture. Corrections have been proposed for this phenomenon and for the constriction of flow due to column wall[3,4], but the above equation appears to work satisfactorily for straight weirs on bubble plates[5].

The weir height is the sum of the skirt clearance, slot height and static submergence. Cap skirt clearance varies from $\frac{1}{2}$ in. for clean services to $1\frac{1}{2}$ in. for trays handling dirty liquids[4]. Slot heights usually used are 1 to $1\frac{1}{2}$ in. Static submergence is provided to ensure that no coning takes place even at very low liquid flow rates across the tray. It varies from zero for vacuum towers, in which pressure drop is an important factor, to $1\frac{1}{2}$ in. for towers operating at 500 p.s.i.g. pressure. For atmospheric towers a seal of $\frac{1}{2}$ in. is found sufficient to prevent coning[6]. Further, the mean dynamic slot submergence is to be of the order of $2\frac{1}{2}$–5 in.[3]

Weir lengths vary from 60 to 80 per cent of the column diameter. A maximum value for liquid height over the weir (h_{ow}) of 1·5 in. is recommended where the weir length is equal to the column diameter or greater; when the weir length is 0·75 times the column diameter, a height of 1·75 in. is taken as the maximum permissible value[5]. For these conditions, the above equation becomes:

$$Q = 333D, \text{ for } h=1{\cdot}5 \text{ and } L=D; \text{ and}$$
$$Q = 415D, \text{ for } h=1{\cdot}75 \text{ and } L=0{\cdot}75D.$$

If the liquid flow rate is greater than that limited by h_{ow} the total may be divided to give 2 or 3 or even 4 flow paths across the deck.

Downspout Capacity and Clearance. The downspout must have sufficient cross-section so that the vapours in the froth flowing down can separate from the liquid and rise up into the vapour space. It has been

found that the terminal velocity of the rise of bubbles in hydrocarbon liquid is about 1 ft/sec.[7] The downcomer cross-section is so sized as to have a velocity in the downcomer varying between 0·6 ft/sec. (for light hydrocarbon services) and 0·3 ft/sec. (for vacuum distillation units)[6]. Another method for sizing downcomer cross-section is based on the residence time. The minimum residence time in the downcomer is 5 sec. calculated on a downflow length equal to the tray spacing[3,4]. Yet another method prescribes that the downcomer cross-section should be such that the height of liquid in the downcomer be not more than 50 per cent of the downflow height[3].

The sheet of liquid flowing over the weir will extend into the downspout, a distance about twice the height of the liquid over the weir. If the downcomers are too narrow, the downflowing liquid will interfere with the upflowing disengaged vapours. Some free width is to be provided for the vapour upflow. For rectangular weirs the width is usually three times the expected liquid height over the weir[5].

A seal is maintained at the bottom of the downcomer to prevent vapour by-pass. A seal of about $\frac{1}{2}$ in. is usually found sufficient[5].

Liquid Level Difference. The difference in level between the clear liquid height at the inlet and that at the outlet weir is known as liquid level difference. Excessive liquid level difference causes back-up of liquid in the downcomers leading to flooding. The gradient across the cap area itself, if excessive, causes poor vapour distribution to the caps.

The liquid level difference across the tray depends on the cap layout, skirt clearance, the liquid and vapour rates.

A large number of investigations have been carried out on the experimental determination of liquid gradients. Fig. 3[6] shows the liquid level difference recommended for use in calculating liquid back-up in downcomers, applicable for 3–6 in. bubble caps. To check vapour distribution, 25 per cent of the liquid level difference as obtained from the figure is used as gradient across the cap field.

Aeration Factor. This is defined as the ratio of observed pressure drop through the liquid on the tray to the calculated clear liquid head.

It has been found that the tray pressure drop does not increase in direct proportion with an increase in clear liquid height on the tray but in lower proportion. This is because of the aeration of the liquid which is a function of the flow rates and properties of the fluids, the static slot submergence and the cap layout.

Fig. 4[6] represents the aeration correction factor as a function of liquid flow rate and the static slot submergence. This form of aeration correction factor is to be subtracted from the sum of the other terms used in calculating the tray pressure drop.

Slot Opening. This is a function of the vapour rate, vapour and liquid densities and the geometry of the slot. Dynamic slot submergence does not have appreciable effect on the slot opening. Winn and Keller[8] present

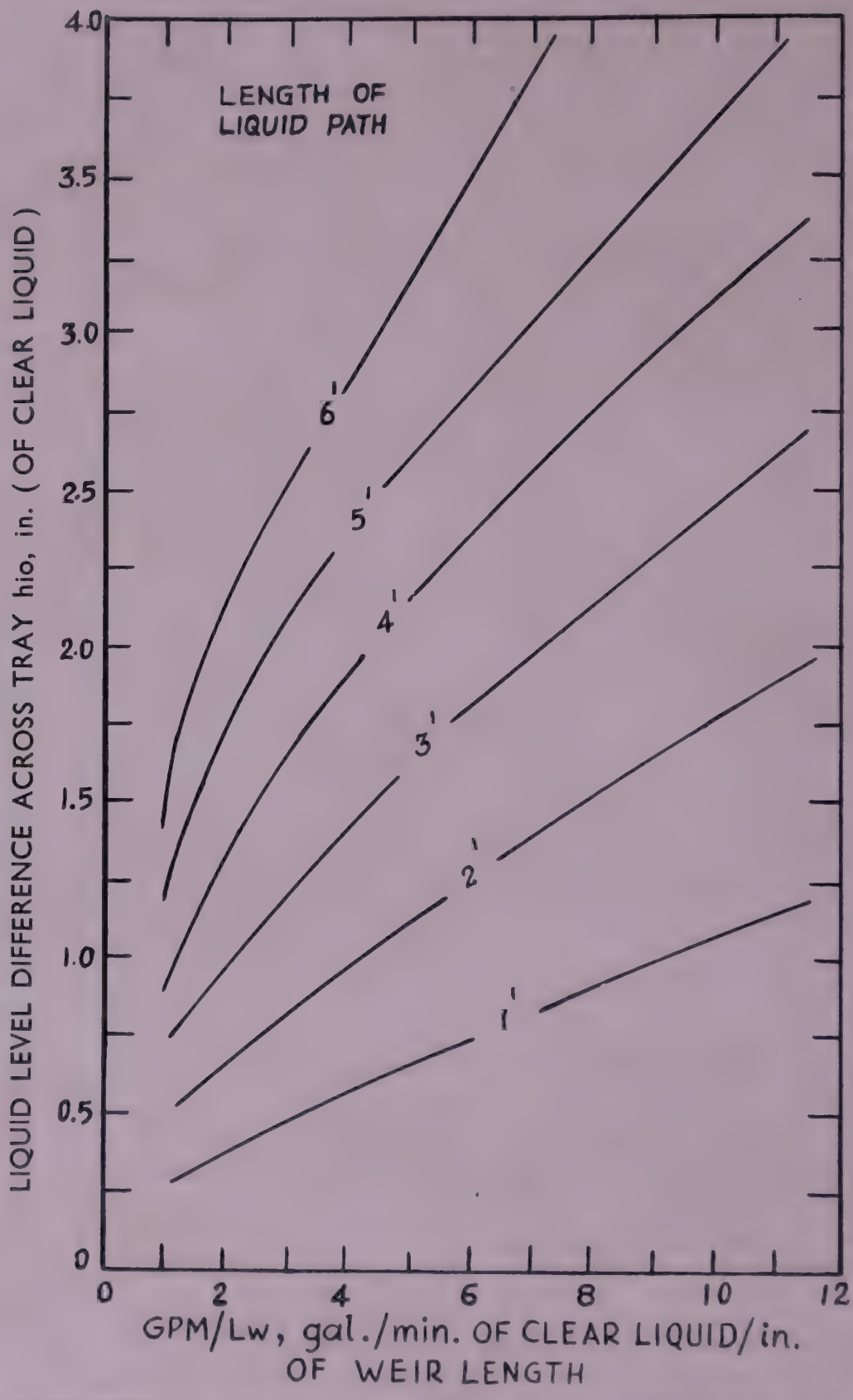

FIG. 3—RELATIONSHIP BETWEEN LIQUID LEVEL DIFFERENCE AND LIQUID BACK-UP IN DOWNCOMERS

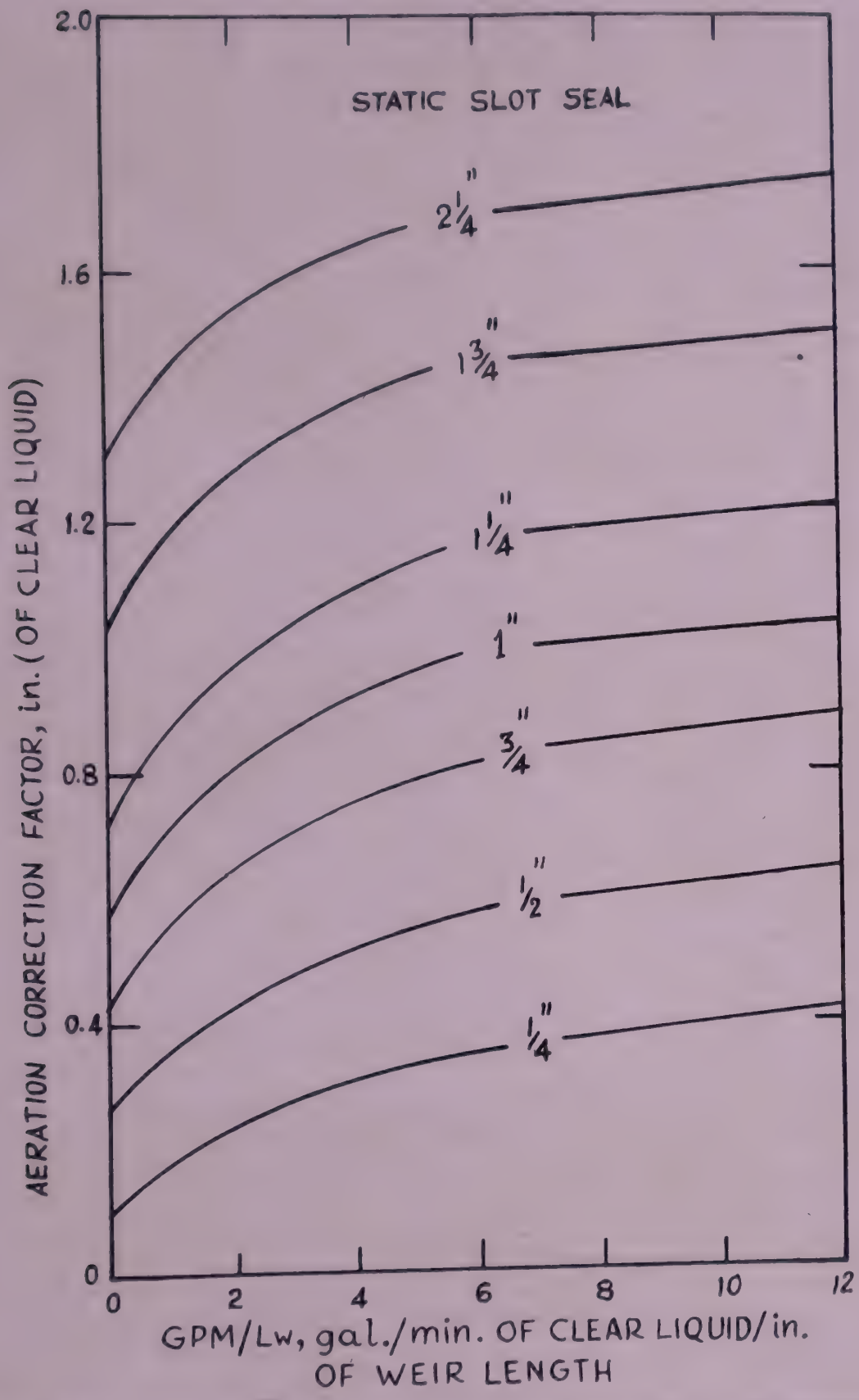

FIG. 4—RELATIONSHIP BETWEEN AERATION CORRECTION FACTOR AND LIQUID FLOW RATE AND STATIC SLOT SUBMERGENCE

nomograms to calculate slot openings from triangular, trapezoidal and rectangular slots. Bolles[3] gives the following equation for determining the capacity of slots:

$$V_m = C_s A_s \sqrt{h_s \frac{(d_l - d_v)}{d_v}}$$

where V_m = vapour rate per tray, cu.ft/sec.,
C_s = coefficient depending on the geometry of slot (0·74 for trapezoidal slots),
A_s = area of slots per tray, sq.in.,
h_s = height of the slot, in., and
d_l, d_v = densities of liquid and vapour.

For any vapour rate, the slot opening may be calculated from this equation. A design rule prescribes that the full slot opening be equal to the slot height at design vapour load and about 0·5 in. at minimum vapour rate to prevent pulsations.

Vapour Distribution. The liquid gradient across the cap field causes uneven distribution of vapours to the caps. The downstream caps having a low submergence will pass more vapours and if the gradient is excessive, the upstream caps may start dumping. The gradient across the cap field is used in conjunction with the wet cap pressure drop to estimate vapour distribution. Dauphine[9] presents a graph for determining the wet cap pressure drop which is the pressure drop through the cap at zero seal (Fig. 5). Bolles[3] prescribes that the ratio of the gradient to wet cap pressure drop should not exceed 0·5 for good vapour distribution. It must be pointed out that the method for calculating the pressure drop through the cap and the gradient by this method is different from other methods and this method should be used *in toto*. If the vapour rates of the inlet and outlet rows of caps differ by more than 30 per cent, stepped caps should be used. The results of Lusk[2] on air-water systems show that the gradient becomes excessive for six or more rows of caps in one plane.

Based on the design principles mentioned above, the quantitative capacity chart may be prepared for a particular tray design.

A similar method for the preparation of capacity charts is presented by Munk[10]. The variables considered in the preparation of the charts are the vapour flow as limited by entrainment and contacting efficiency, the liquid flow as limited by the downspout capacity, the relative effect of vapour and liquid flow rates on the stability of tray operation and on vapour distribution and the size of caps, layout, etc.

The emphasis is on the velocity through caps as limited by entrainment rather than on the superficial velocity through the column. The capacity

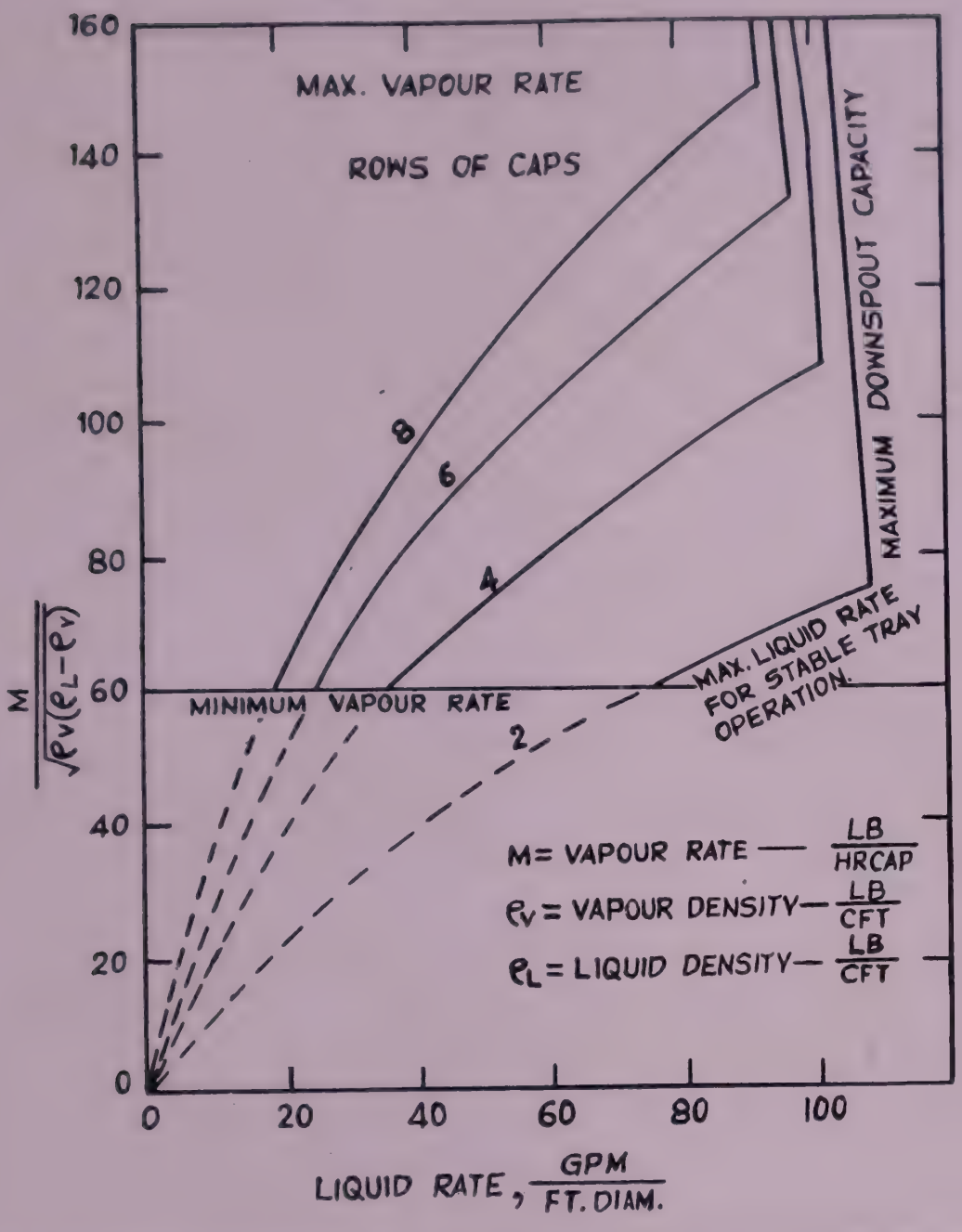

FIG. 5—VAPOUR AND LIQUID RATE LIMITATIONS FOR STANDARD BUBBLE CAP TRAYS WITH 24 IN. TRAY SPACING

curve for a 4 in. bubble cap stray on 24 in. plate spacing and with a weir length 75 per cent of the column diameter is shown in Fig. 6[5].

Operation conditions that come inside the approximately triangular space limited at the top by the value of

$$\frac{M}{[\rho_v\ (\rho_1-\rho_v)]^{\frac{1}{2}}} = 160, \text{ and above the line } \frac{M}{[\rho_v\ (\rho_1-\rho_v)]^{\frac{1}{2}}} = 60$$

and to the left of the curved line representing the number of rows of caps may be expected to work satisfactorily.

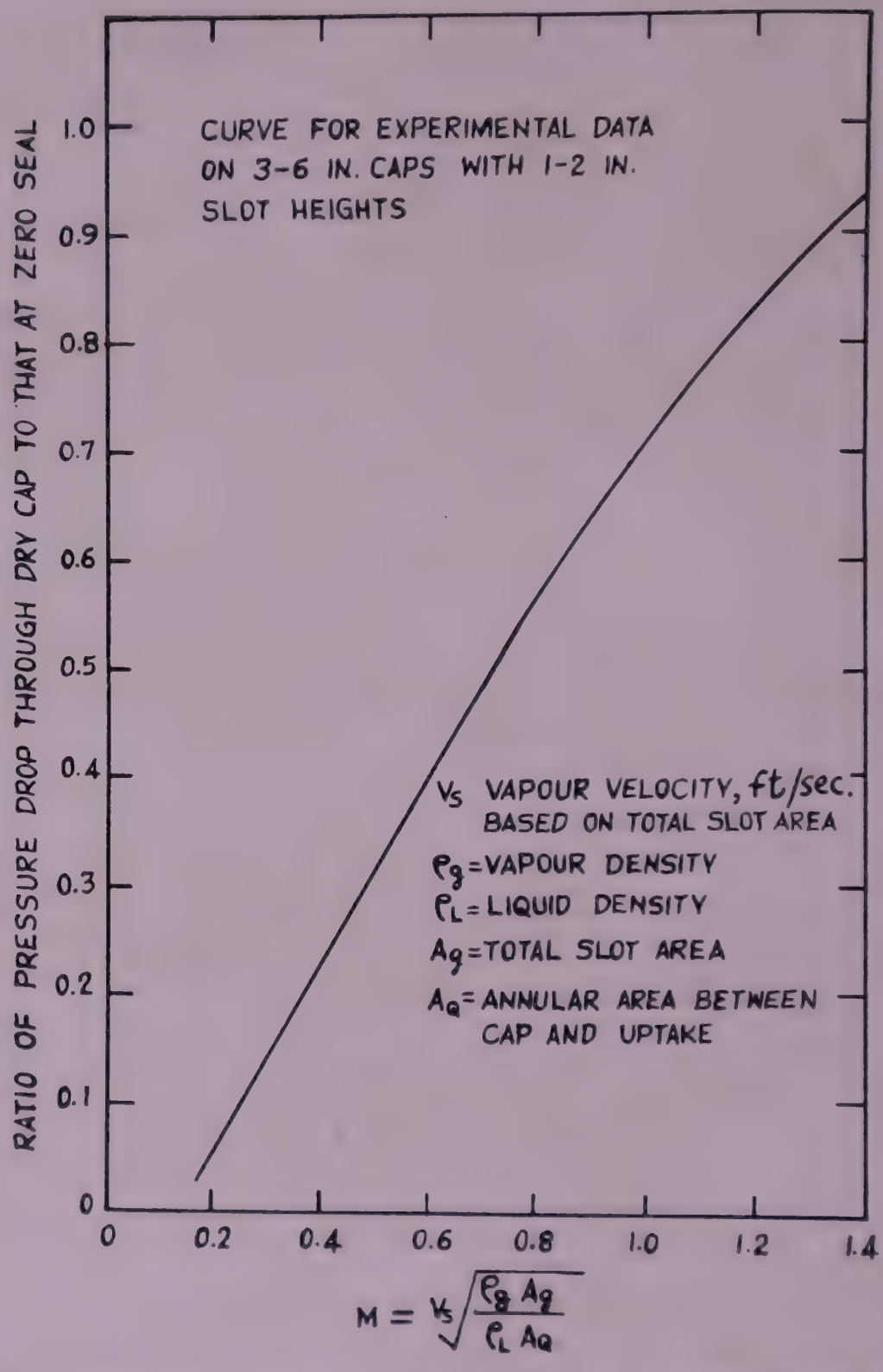

FIG. 6—CAPACITY CURVE FOR A 4 IN. BUBBLE CAP TRAY ON 24 IN. PLATE SPACING AND WITH A WIER LENGTH OF 75 PER CENT OF THE COLUMN DIAMETER

While such charts may be prepared for a particular tray, it does not represent an optimum design. Modifications could be carried out in the same tray to increase the capacity or reduce the cost. Again, the optimum tray design for one type should be compared with that of various other types to arrive at the most economic tray design for a particular service.

COMPARATIVE CAPACITIES AND COSTS OF VARIOUS TRAYS

Sieve Tray. The chief merits of a sieve tray over a bubble cap tray are that it has a higher capacity for the same column diameter and the cost is considerably less. Typical hydrocarbon service columns show 10–40 per cent greater capacity[11]. Cost varies from 25 to 70 per cent of that of bubble cap trays. Sieve trays show a flatter efficiency curve and the efficiency exceeds that of bubble cap trays by 5–15 per cent.

Uniflux Tray. It may be considered as an improved version of the bubble cap tray. Fractionating efficiencies appear to hold remarkably well even at rates 40–70 per cent above design[12]. Tower diameters would be the same as for conventional bubble caps but trays are light in weight (8 lb./sq. ft of superficial tower area). They are claimed to cost 40–60 per cent as much as bubble cap trays excluding the cost of shell[11].

Flexitray. The capacity of a flexitray in common hydrocarbon services is 12–50 per cent higher than for bubble cap trays. Column efficiencies are about 10–20 per cent higher than those of bubble trays[13] and these efficiencies are constant over a considerable range of flow rates. They seem to function particularly well in absorber services where the efficiencies are in the range of 70–90 per cent compared to 25–30 per cent in bubble trays. Prices, excluding shell cost, are 60–80 per cent of those of bubble trays[11,13].

Float Valve Tray. Capacity, efficiency and cost of float valve trays are about the same as those of a flexitray.

Turbogrid Tray. Turbogrid trays have 20–100 per cent greater capacity and the same separating efficiency per foot of tower height as bubble cap trays. Pressure drops are 40–80 per cent less[14]. Costs vary between 55 and 75 per cent of those of bubble trays for small diameter columns and the saving is much more for towers of diameters exceeding 7 ft[11].

Ripple Tray. The wave pattern of a ripple tray makes it structurally strong and the trays can be fabricated from much thinner plates than required for a perforated tray. They are usually made of stainless steel since the difference in cost between a carbon steel plate and a stainless steel plate is very small. Efficiencies for certain services are reported to be 25 per cent higher[15]. Capacity and cost should be about the same as those of a perforated tray.

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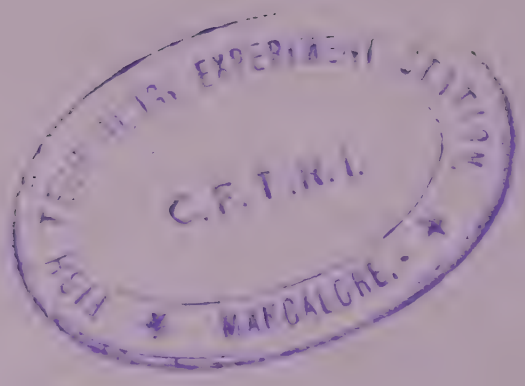

Separation by Sweep Distillation

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The principle of sweep distillation has been applied to cross the azeotropic compositions in the case of the systems, ethyl alcohol-water and pyridine-water. The vapours of these systems are allowed to diffuse through a diaphragm into an inert gas (air) in a countercurrent manner and the inert gas stream and vapour mixture stream are analysed. An expression connecting the diffusivity and mole per cent of the key component in vapour and liquid phase has been derived and applied for calculating the composition of vapour. The influence of pressure, rates of gas and vapour streams and column dimensions on enrichment have been studied. The results have shown that the method can be successfully employed to cross the azeotropic points.

A number of diffusion processes like sweep diffusion, mass diffusion and gaseous diffusion are used in the separation of gases from one another, like hydrogen from nitrogen or carbon monoxide[1], nitrogen or hydrogen from carbon dioxide[2], helium from helium-neon mixture[3] and in the separation of isotopes. An attempt has been made in the present investigation to apply the principle of sweep distillation for crossing the azeotropic composition in cases of binary azeotropes. One of the usual methods of separating azeotropic mixtures is by the addition of a suitable third component and distilling it, as in the case of azeotropic and extractive distillations. This method of sweep distillation has an advantage over others in that this method does not require the addition of a third component. Further, this is a general method useful for the separation of all types of azeotropic mixtures.

In this method a mixture of vapours of two substances is separated, or the components are enriched by using the difference in their diffusivities into an inert gas (air, hydrogen, nitrogen, etc.) which does not react with either of the vapour components. The vapour mixture is allowed to diffuse through a diaphragm into the inert gas in a countercurrent manner. The lighter component diffuses faster into the inert gas than the heavier component. As a result of this, the inert gas stream carries with it a higher per cent of the lighter component and the vapour mixture stream carries with it a higher per cent of the heavier component. The products are separately condensed and analysed for finding out the degree of separation.

This method has been applied for effecting separation in the two azeotropic systems, ethyl alcohol-water forming an azeotrope at 89·4 mole per cent or 95·6 per cent by weight of alcohol at a pressure of 760 mm. of

mercury and pyridine-water system forming an azeotrope at 25 mole per cent or 57 per cent by weight of pyridine at a pressure of 760 mm. of mercury which were investigated at the atmospheric pressure prevailing at Bangalore (680–690 mm. of mercury). A noncondensable gas, namely, air was used as the carrier.

EXPERIMENTAL SET-UP

The set-up consists of a still for the generation of vapour, a superheater and the main diffusion column on one side and an air drying set-up and an air preheater on the other side as shown in Fig. 1. The main diffusion column is shown in Fig. 2. The vapour generated from an azeotropic liquid was preheated to a fixed temperature and was admitted on the outer side of the diaphragm. Dry preheated air was passed countercurrent to the vapour stream on the inner side of the diaphragm. The pressures of vapour and air were noted in the manometers.

The pressure of vapour was controlled by means of a relay connected to the still heater. The pressures on both sides of the diaphragm were controlled by manipulating valves on the outlet side of air and vapour streams. To avoid condensation either at the lead lines or at the diaphragm, the whole diaphragm column and the lead lines were electrically heated and the set-up was completely lagged.

Diffusion occurred, and as a result air stream carried with it more of water vapour of the systems, while the vapour stream was enriched with respect to the other components. The two streams were separately condensed in coiled condensers immersed in ice-salt mixture. The condensate was removed after each run, and the samples were weighed and analysed.

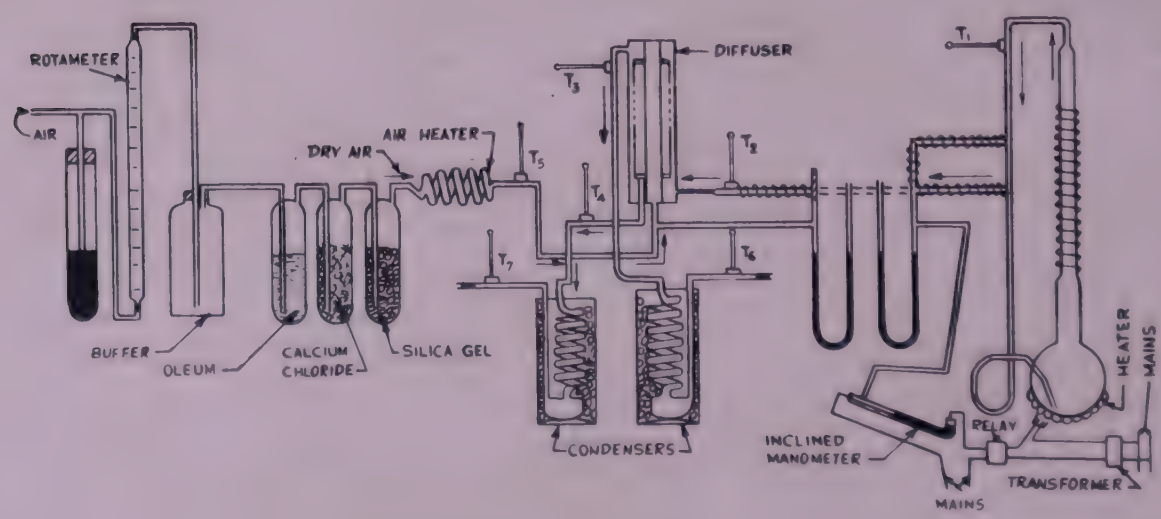

FIG. 1—SET-UP FOR STUDIES ON SWEEP DISTILLATION

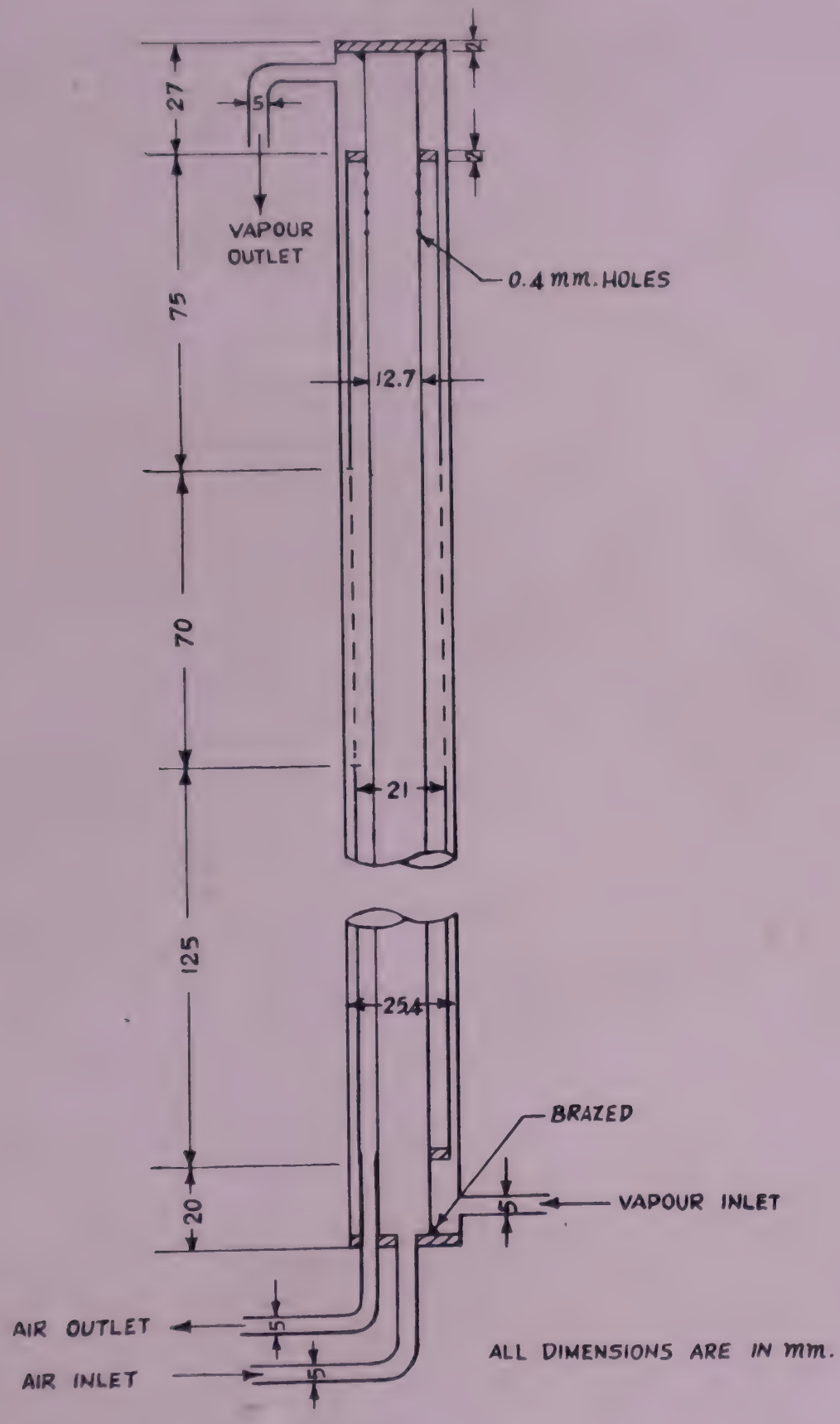

FIG. 2—DIFFUSION COLUMN

METHODS OF ANALYSIS

The concentration of alcohol was estimated by a calorimetric method[4]. The method is based on the principle that the sensitivity of azo indicators, (for example, methyl orange) to acid diminishes with increasing alcohol concentration. Making use of alcohol samples of known concentrations a calibration curve of concentration versus per cent of light transmitted was prepared. To analyse unknown samples, the required quantity of acid and indicator were added to the samples and the percentage of light transmitted was read out in a colorimeter. The corresponding concentrations of alcohol were obtained from the calibration curve. In the range of concentration of alcohol 92–100 per cent by weight the maximum error that can occur in this method is $\pm$ 0·2 per cent.

The analysis of pyridine was based on the fact that it precipitates an equivalent amount of ferric hydroxide from ferric chloride, and this quantity of ferric hydroxide can be determined by titrating it against standard sulphuric acid[5]. The maximum error that can occur in this analysis is $\pm$2·0 per cent by weight.

THEORETICAL CONSIDERATIONS

Considering diffusion of ethyl alcohol or pyridine vapour and water vapour into air, the enrichment factor γ can be put as[6]

$$\gamma = \frac{D_{0_1} - D_{0_2}}{D_0} \qquad (1)$$

where

D_{0_1} = diffusivity of water vapour into air,

D_{0_2} = diffusivity of ethyl alcohol or pyridine vapour into air,

$D_0 = \frac{D_{0_1} + D_{0_2}}{2}$, and

γ = enrichment factor.

The diffusivity or diffusion coefficients of these vapours into air can be calculated by using Arnold's[7] or Gilliland's[8] or Hirschfelder's[9] equations. The diffusion coefficients for the present investigation were calculated, using Arnold's equation as this was found to be quite accurate and comparatively easy. The molecular volumes of the components were calculated using Kopp's rule of additive volumes and Le Bas values given in literature[10].

$$D_{12} = \frac{0.000837.T.^{5/2}\,[(M_1+M_2)/(M_1-M_2)]^{1/2}}{P.\,(V_{b_1}^{1/3}+V_{b_2}^{1/3})^{2}\,(T+S_{12})} \qquad (2)$$

where

D_{12} = diffusivity of one vapour into another,

T = absolute temperature (°K.) at which diffusivity is desired,

M_1 & M_2 = molecular weights of components,

V_{b_1} & V_{b_2} = molecular volumes of the components at their normal boiling points, and

S_{12} = Sutherland's constant.

Sutherland's constant is obtained from Equation (3)

$$S_{12} = 1{\cdot}47\ F\sqrt{T_{b_1}\ T_{b_2}} \qquad (3)$$

where F is a constant and

T_{b_1} and T_{b_2} are normal boiling temperatures (°K.) of the components 1 and 2.

The value of F can be obtained from the chart given in literature[11] where F is plotted against the ratio of molecular volumes of components 1 and 2.

The enrichment factor γ is related to the equilibrium separation factor by the equation

$$\alpha = \gamma + 1. \qquad (4)$$

For a two-component system,

$$\alpha = \frac{y/(1-y)}{x/(1-x)} \qquad (5)$$

where

y = mole per cent of key component in the vapour phase, and

x = mole per cent of key component in the liquid phase.

Combining Equations (1), (4) and (5):

$$\frac{D_{0_1}-D_{0_2}}{D_0} + 1 = \frac{y/(1-y)}{x/(1-x)} \qquad (6)$$

Using Equation (6), the vapour composition of a system can be calculated by substituting the values for feed compositions and diffusion coefficients.

RESULTS AND DISCUSSION

The calculated values for the compositions of the enriched phases of alcohol and pyridine from Equation (6) and diffusivities as calculated from Equation (2) and the temperature of operation are given in Table 1.

It will be seen from Table 1, that in one stage, for alcohol-water system, the alcohol composition increases from azeotropic composition to 97·3 per cent by weight of alcohol and for pyridine-water system, the pyridine composition increases from azeotropic composition to 73·8 per cent by weight of pyridine, at the operating temperature and pressure, under ideal conditions.

The following operating variables were studied: pressure of operation; column dimensions; and pressure difference across diaphragm. The effect of these variables is discussed below.

Pressure of Operation. When the pressure external to the diaphragm is increased, molecules of components of the mixture come closer and increases the extent of mixing and hence the extent of separation is decreased.

In this investigation pressure was noted in a manometer with kerosene as the manometric liquid. Kerosene was used, as it is immiscible with water, pyridine and with alcohol to some extent, and also because it is a light liquid and can give fairly accurate reading of the pressures. Some typical results obtained with regard to the systems alcohol-water and pyridine-water, are represented graphically in Figs 3 & 3a and Figs 4, 4a & 4b respectively.

It will be observed that for both the systems, generally the extent of separation goes down with increase of operating pressure at various ratios of sample from vapour side to air side. However, the change in concentration is small because of the limited range of variations of pressures.

TABLE 1—DIFFUSIVITIES OF COMPONENTS AT OPERATING TEMPERATURES AND COMPOSITION OF THE TWO STREAMS

Mixture	Diffusivity *sq. cm./sec.*	Temperature °K.	Equilibrium separation factor (α)	Composition of feed, %		Vapour side composition, %	
				Mole	Wt	Mole	Wt
Alcohol	0·166	363		89·4	95·6	93·4	97·3
+			1·677				
Water	0·336	363		10·6	4·4	6·6	2·7
Pyridine	0·132	373		25·0	57·0	39·1	73·8
+			1·929				
Water	0·360	373		75·0	43·0	60·9	26·2

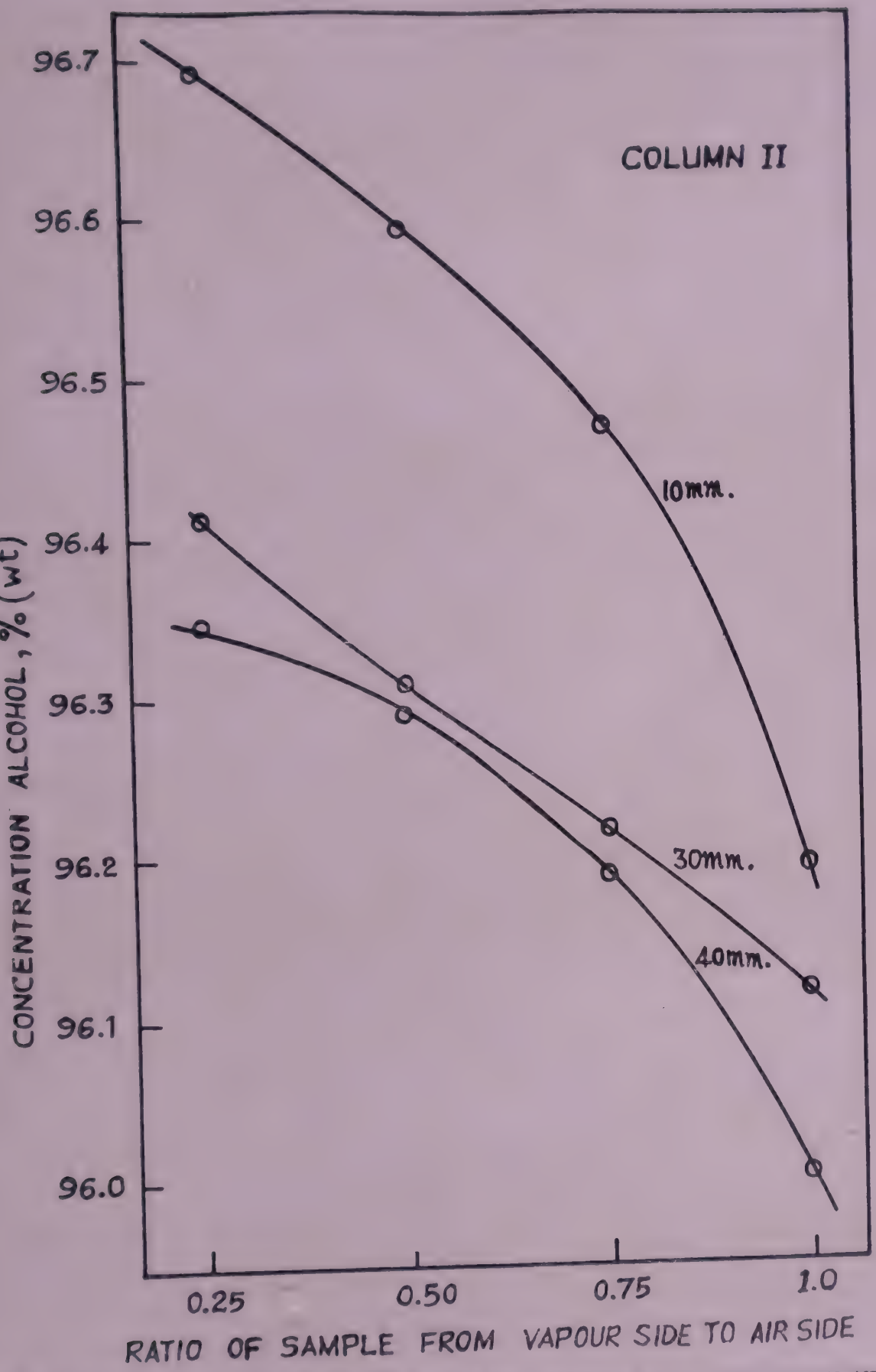

FIG. 3—EFFECT OF PRESSURE OF OPERATION AND RATIO OF SAMPLE FROM VAPOUR SIDE TO AIR SIDE ON CONCENTRATION (ALCOHOL-WATER SYSTEM)

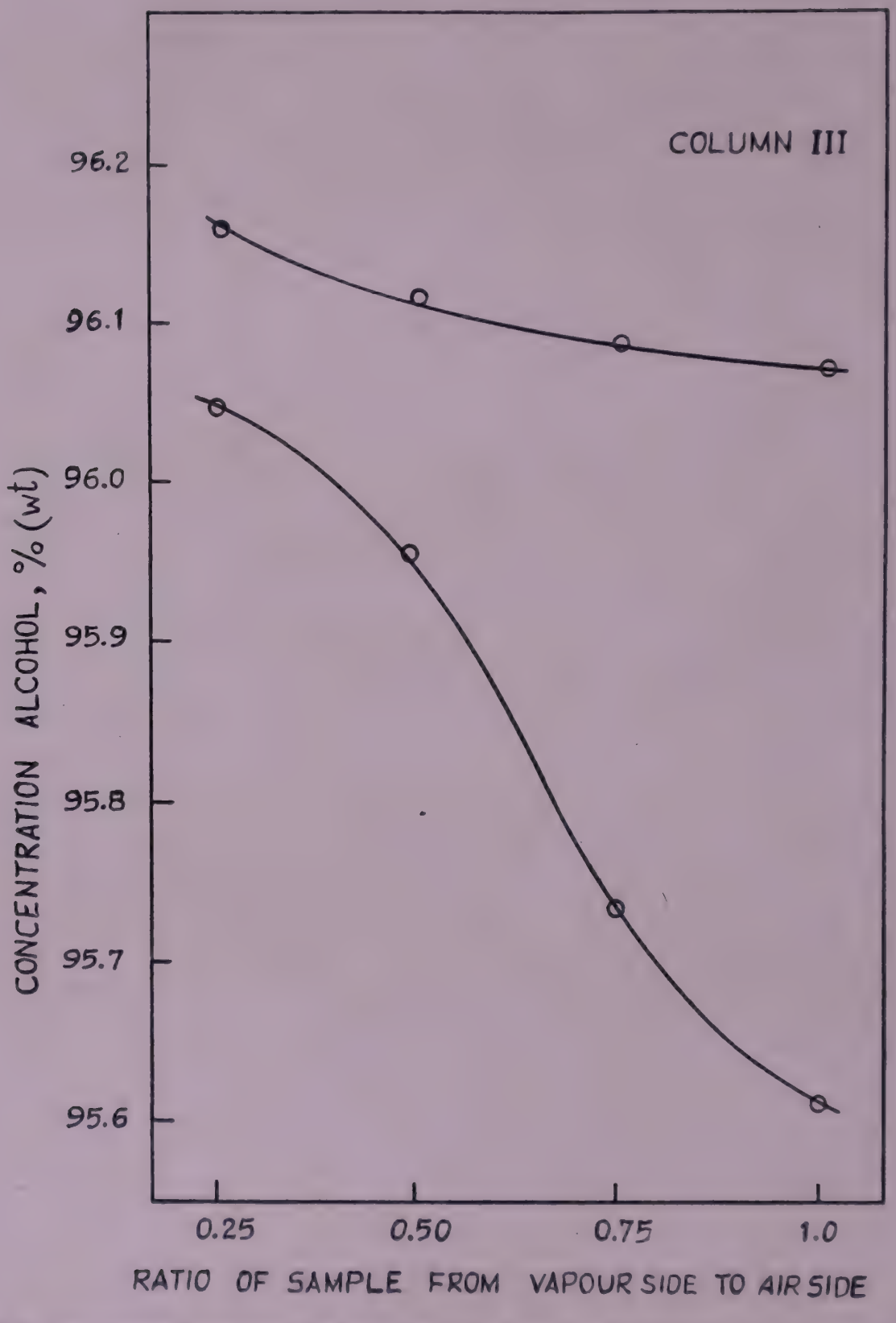

FIG. 3a—EFFECT OF PRESSURE OF OPERATION AND RATIO OF SAMPLE FROM VAPOUR SIDE TO AIR SIDE ON CONCENTRATION (ALCOHOL-WATER SYSTEM)

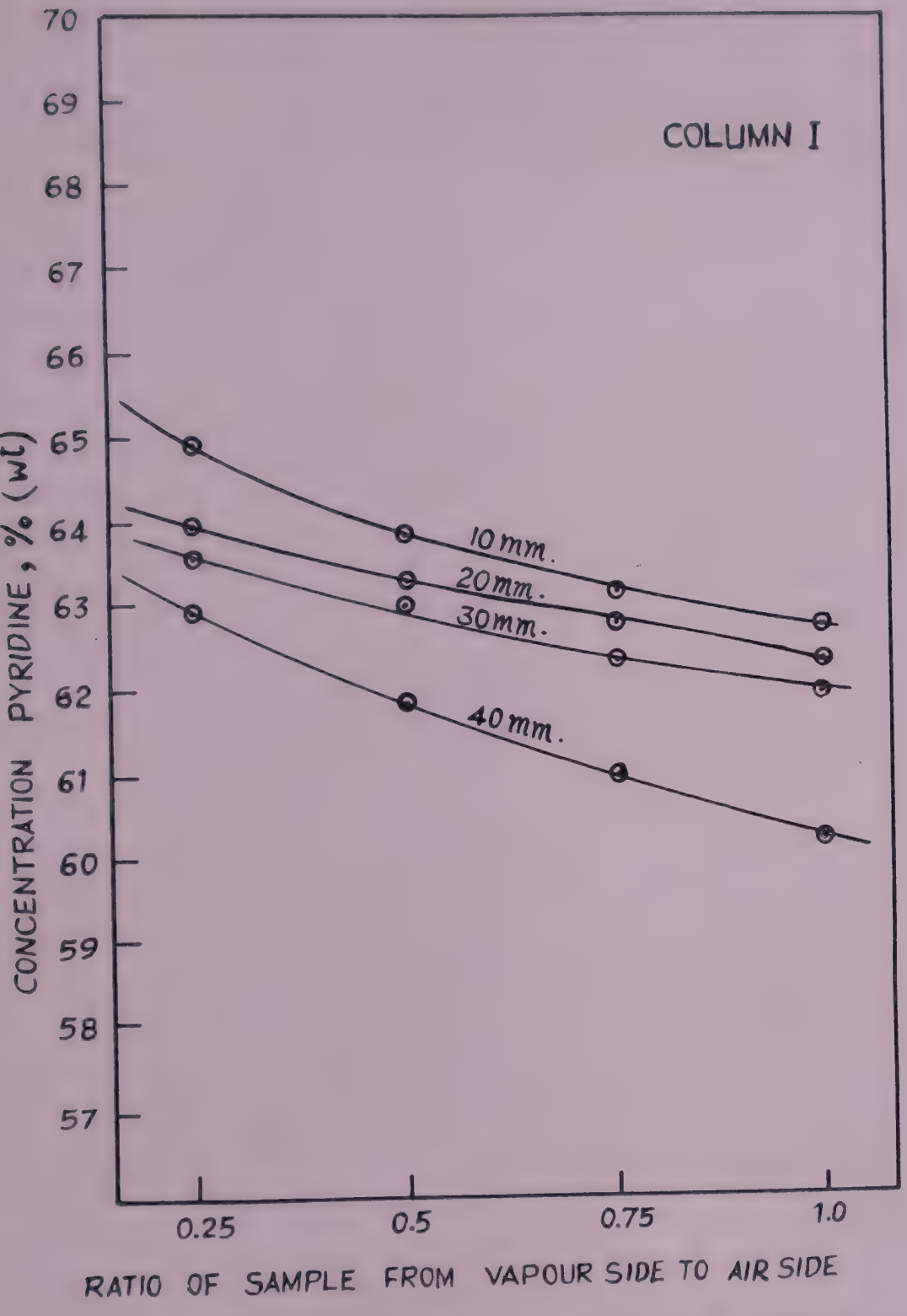

FIG. 4—EFFECT OF PRESSURE OF OPERATION AND RATIO OF SAMPLE FROM VAPOUR SIDE TO AIR SIDE ON CONCENTRATION (PYRIDINE-WATER SYSTEM)

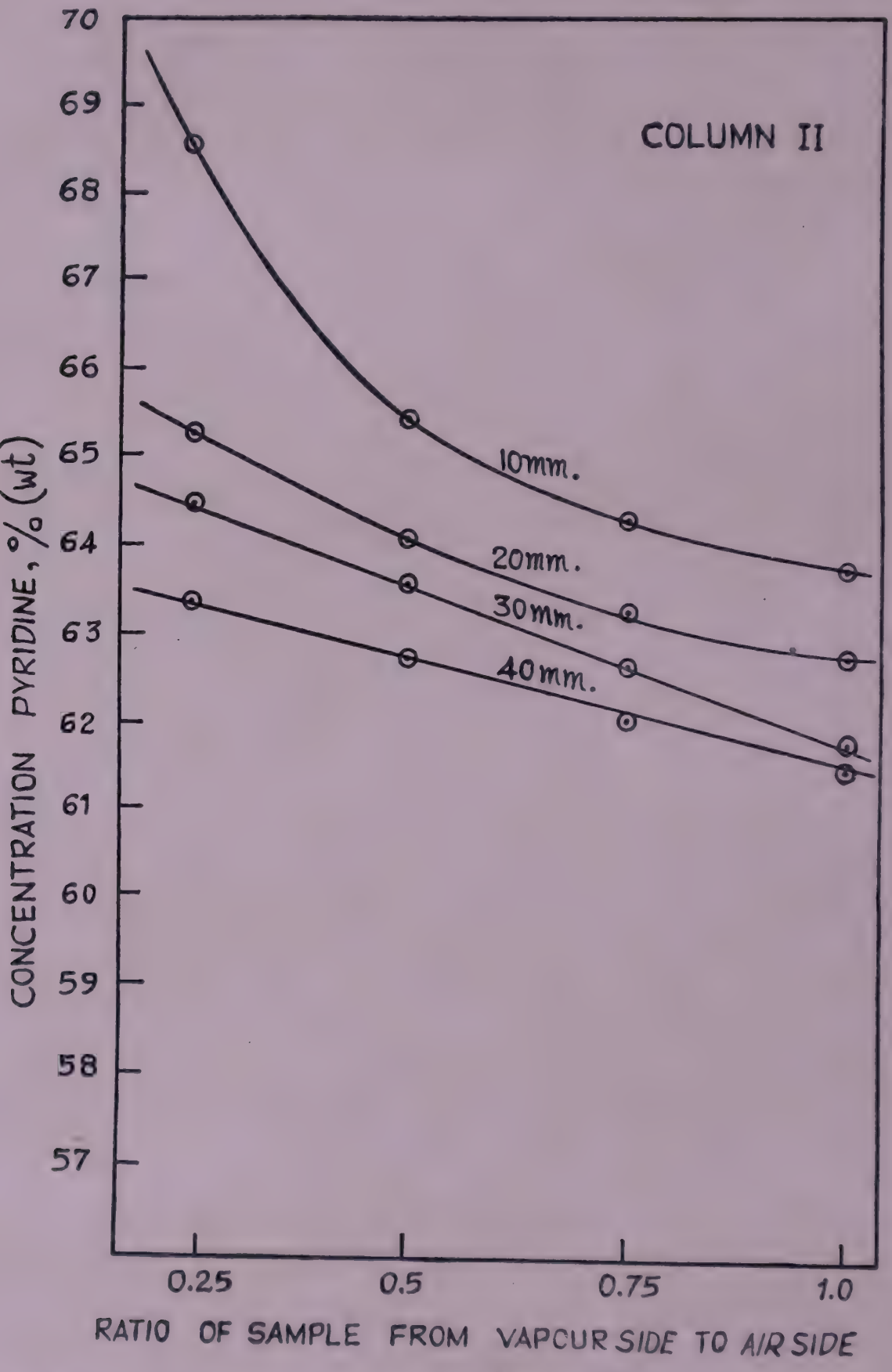

FIG. 4a—EFFECT OF PRESSURE ON OPERATION AND RATIO OF SAMPLE FROM VAPOUR SIDE TO AIR SIDE ON CONCENTRATION (PYRIDINE-WATER SYSTEM)

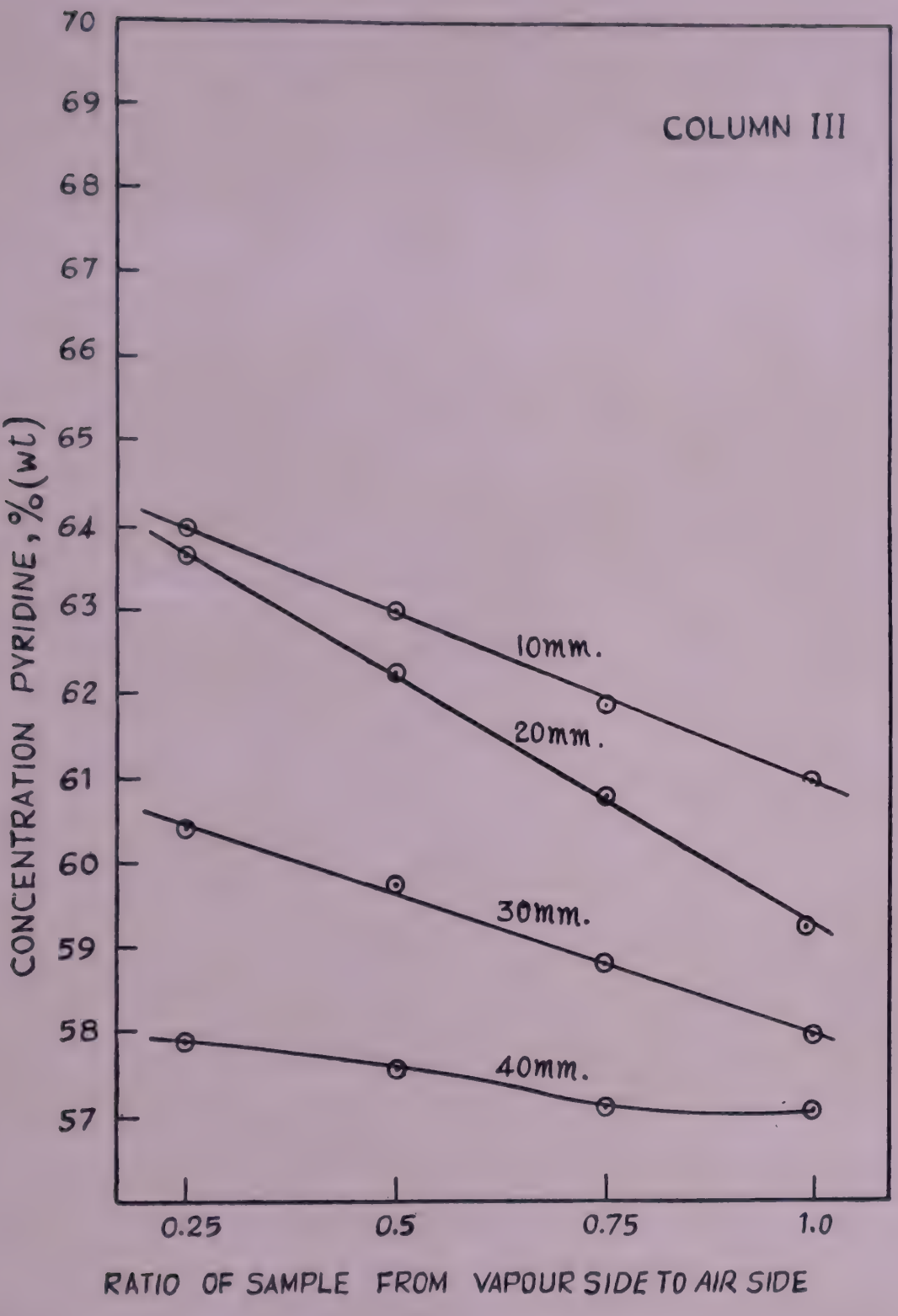

FIG. 4b—EFFECT OF PRESSURE ON OPERATION AND RATIO OF SAMPLE FROM VAPOUR SIDE TO AIR SIDE ON CONCENTRATION (PYRIDINE-WATER SYSTEM)

Column Dimensions. The main dimension that might affect the separation factor is the screen area exposed for diffusion. The greater the area exposed for diffusion the greater is the change of the vapour to come into equilibrium with air and hence the increase in enrichment. The effect of screen area was studied with three columns. The dimensions of the diaphragms and other constructional details are given below:

	Column I	Column II	Column III
Diameter, *mm.*	21	21	21
Length, *mm.*	70	200	40
Area, *sq. cm.*	46·2	132	26·4

The diaphragm in all cases was fabricated out of phosphor bronze market variety wire mesh measuring 0·0508 mm. square aperture.

TABLE 2—EFFECT OF COLUMN DIMENSIONS ON COMPOSITION: ALCOHOL-WATER SYSTEM

(*Pressure, atm. pressure at Bangalore* +10 *mm. of kerosene; temp.*, 85-90°*C.*)

Ratio of sample from vapour side to air side	Weight % of alcohol in vapour side of		
	Column I	Column II	Column III
0·25	96·30	96·70	96·13
0·50	96·10	96·60	96·10
0·75	96·00	96·48	—
1·00	96·00	96·20	—

TABLE 3—EFFECT OF COLUMN DIMENSIONS ON COMPOSITION: PYRIDINE-WATER SYSTEM

(*Pressure,* 680-685 *mm. of Hg* +10 *mm. of kerosene; temp.*, 95-100°*C.*)

Ratio of sample from vapour side to air side	Weight % of pyridine in vapour side of		
	Column I	Column II	Column III
0·25	65·00	68·60	64·00
0·50	63·90	65·40	63·10
0·75	63·20	64·40	61·90
1·00	62·80	63·80	61·00

It will be seen from Figs 3, 3a and 4, 4a, 4b that for both the systems, the extent of enrichment of alcohol and pyridine, using column II, having more screen area exposed for diffusion is more, and that the difference of weight per cent of alcohol and pyridine using all the columns decreases, as the ratio of sample from vapour side to air side is increased.

Pressure Difference across Diaphragm. Diffusion occurs on both sides of the diaphragm; hence a slight increase in pressure on one side will cause the movement of the molecules of components from that side to the other side and hence tremendous amount of mixing of molecules of different components will occur. This results in the decrease in enrichment.

The ratio of sample from vapour side to air side is indicative of the pressure difference across the diaphragm. When the pressure increases on the vapour side, more vapour tries to pass into the air and hence the ratio is reduced, whereas if the pressure on the air side is increased, air comes along with the vapour and the ratio is increased. Results obtained for the various ratios showing the weight per cent of alcohol and pyridine in the two systems with the three different columns are given in Tables 2 and 3 respectively.

It was observed that when the pressure on vapour side is increased, maximum enrichment was obtained, but the amount of sample collected on the vapour side was very small.

This method of sweep distillation has the definite advantage in that by the inclusion of a diffusion column (of the design described in this paper) in between the distillation column and the condenser, enriched components are obtainable from azeotropic composition of the components. A flow sheet for such a set up is given in Fig. 5.

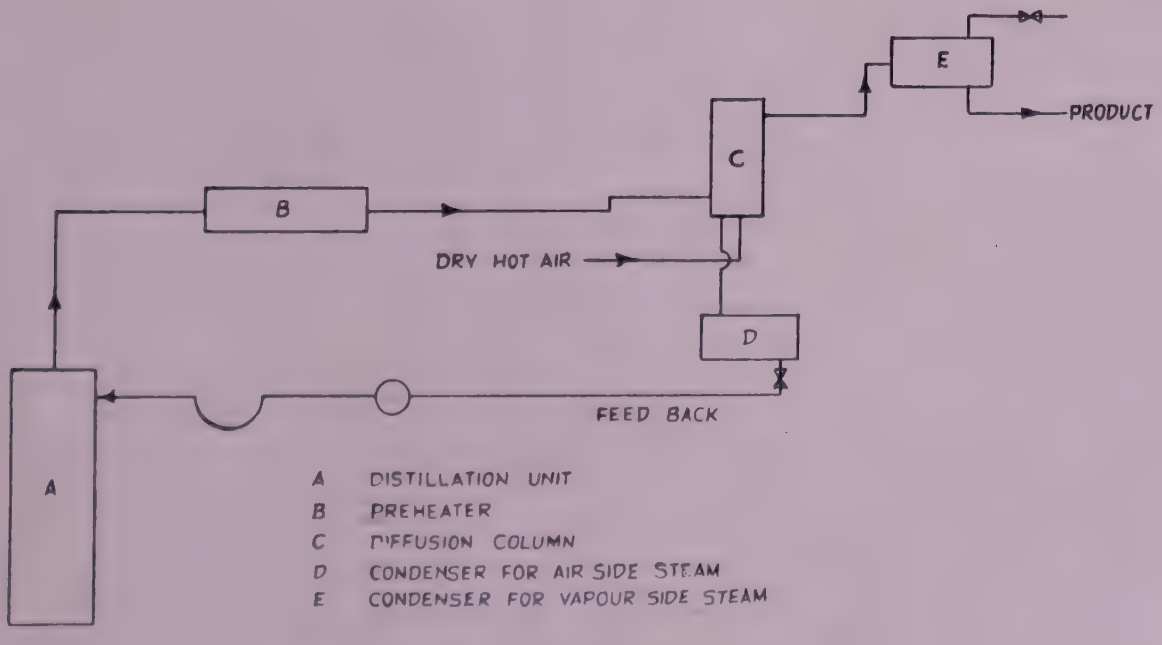

FIG. 5—FLOW SHEET FOR SWEEP DISTILLATION

Vapour stream, say of azeotropic composition, coming out of the distillation column A, is admitted to the diffusion column C, after being passed through the superheater B. Air or any other suitable inert gas stream is allowed inside the diffusion column C, and the two streams, namely of vapour and of air, are passed through two separate condensers (E, D)—the condensate from the former giving the enriched product, whereas, the condensate from the latter, depleted with respect to the desired component, is fed back to a suitable position in the distillation column where the composition at the plate is equal to the composition of the feed back. In this way, an enriched product beyond azeotropic composition is obtainable in a single set-up, which includes essentially an additional diffusion column with the distillation column.

Acknowledgement

Thanks are due to Prof. N. R. Kuloor for his encouragement during the progress of the work reported in this paper.

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Prediction of Local Plate Efficiency

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A correction factor which accounts for the transfer process during the formation of a spherical bubble at the slot of a distillation plate has been derived and incorporated in the general expression for the gas film mass transfer coefficient. This enables the local plate efficiency to be estimated with greater precision.

Several attempts have been made in the past to derive expressions for the local plate efficiency in a distillation column from a knowledge of the physical and geometric properties of the system. Geddes[1] assumed that the bubbles released from the slots were spherical and derived the following equation:

$$E=1-exp\left(\frac{6\ K_g t}{d_o}\right). \tag{1}$$

The same equation may be directly utilized for the evaluation of the local efficiency, provided the gas film and liquid film mass transfer coefficients are known. These coefficients may then be combined to provide the overall mass transfer coefficient, K_g, according to the following relationship:

$$\frac{1}{K_g}=\frac{1}{k_g}+\frac{m}{k_L}. \tag{2}$$

The liquid film transfer coefficient, k_L, may be evaluated from an equation derived by Higbie[2]:

$$k_L=\left(\frac{4D_L}{\pi t}\right)^{\frac{1}{2}}. \tag{3}$$

Barrer[3] derived an expression for the gas film transfer coefficient, k_g, based on the assumption of unsteady state diffusion, with spherical symmetry, inside the spherical bubble:

$$k_g=-\frac{d_o}{6t}ln\left[\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}exp\left(\frac{-n^2\pi^2 D_m t}{\left(\frac{d_o}{2}\right)^2}\right)\right] \tag{4}$$

The above equation defines the transfer coefficient pertaining to the mass transfer process only after the spherical bubble is released into the flowing medium. It is generally accepted that a substantial fraction of the total mass transfer taking place during the life-time of a spherical bubble occurs during the formation of the bubble at the slot. While it is very difficult to assess accurately the extent of mass transfer during this formative period owing to the complicated nature of the process, an approximate corrective term may be incorporated in Equation (4) to account for the transfer during bubble growth.

If it is assumed that mass transfer by eddy diffusion is the predominant mechanism during bubble growth, it is possible to obtain a correction factor of the form $E_m \cdot (t/d^2_o)_{av.}$ to take care of the changing diameter (which is a function of time), and hence the surface area of, the growing bubble. This term can then be incorporated in the exponential term of the simplified form of Equation (4). The following analysis will be concerned with a distillation plate in a sieve plate column. Let the vapour rate through the column be V_m lb. moles/hr and let there be m_o orifices through which this quantity of vapour is released into the flowing liquid. The diameter of each bubble, d_o, at the time of its release may be evaluated from the following equation developed by Van Krevelen[4]:

$$d_o = \left[\frac{72\ V^2 \rho_L}{\pi^2\ g\ (\rho_L - \rho_g)}\right]^{\frac{1}{5}} \tag{5}$$

The time of formation of the bubble, t_f, may be estimated as the ratio of the volume of the individual bubble to the volumetric vapour rate through an individual orifice. It may be given by the following equation:

$$t_f = \frac{m_o \pi d_o^3}{6\beta V_m} \tag{6}$$

where β is the correction factor for changing lb. moles into cu. ft.

At any time during the formation of the bubble, the diamter of the growing bubble may be related to the time of formation, t, by the following equation:

$$d = \left(\frac{6\beta V_m t}{m_o \pi}\right)^{\frac{1}{3}} = at \tag{7}$$

where a is a constant and equals $\left(\frac{6\ \beta\ V_m}{m_o \pi}\right)^{\frac{1}{3}}$.

The time averaged term, $E_m(t/d_o^2)$, may be given by the integral:

$$E_m\,(t/d^2)_{av.} = \frac{E_m}{t_f}\int_0^{t_f} \frac{t}{d^2}\,dt = \frac{E_m}{a^2\,t_f}\int_0^{t_f} t^{\frac{1}{2}}\,dt \tag{8}$$

$$= \left(\tfrac{3}{4}\,E_m\,\frac{t_f}{d_o^2}\right). \tag{8a}$$

The correction factor $\frac{3}{4}E_m(t_f/d_o^2)$ may then be incorporated in the simplified expression for mass transfer coefficient involving only the first term in the series. The true gas film transfer coefficient may be given by the following expression:

$$k_g = \frac{d_o}{6t}\left[\frac{4\,\pi^2\,D_m\,t}{d_o^2}\left(1+\tfrac{3}{4}\,\frac{E_m}{D_m}\right) - ln\,\frac{6}{\pi^2}\right]. \tag{9}$$

Considering the correction term inside the curved bracket in Equation (9), the ratio of the time of formation of the bubble to that of its ascent may be of a small order of magnitude; but the ratio of eddy mass diffusivity to the molecular diffusivity may be large enough to make the correction factor assume appreciable importance in the evaluation of the true gas film mass transfer coefficient. It is a different problem, of course, to estimate the magnitude of the eddy diffusion coefficient. However, the necessity for revision in the existing equation for providing the true mass transfer coefficient must be recognized.

Nomenclature

d = Bubble diameter, ft
d_o = Bubble diameter on its release, ft
D_L = Liquid diffusivity, ft²/hr
D_m = Gaseous diffusivity, ft²/hr
E = Local efficiency
E_m = Eddy diffusivity, ft²/hr
g = Acceleration due to gravity
K_g = Overall mass transfer coefficient, ft/hr
k_g = Gas film mass transfer coefficient
k_L = Liquid film mass transfer coefficient
m = Slope of equilibrium curve
m_o = Number of orifices in the plate
t = Time, hr

t_f = Time of formation of bubble, hr
V_m = Vapour flow rate, lb. moles/hr
β = Conversion factor for converting lb. moles into cu. ft
ρ = Density

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Estimation of Hold-up in Packed Liquid-Liquid Extraction Columns at and below Flooding

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Estimation of hold-up in packed liquid-liquid extraction columns is necessary for predicting their performance for mass transfer operations. Hence, using a 3 in. extraction tower of glass the hold-up below flooding has been estimated. Agreement has been found between these results and the generalized correlation arrived at by Sitaramayya and Laddha. A new generalized correlation has also been derived for estimation of the hold-up at flooding in packed liquid-liquid extraction towers.

In the operation of the liquid-liquid extraction columns it is found that a definite amount of the dispersed phase is always present in the interstices of the packing and the amount of the dispersed phase thus held up in the column is dependent upon the flow rates of the two phases in the column. The ratio of the amount of the dispersed phase (on volume basis) present in the interstices of the packing between the interface and the packing support in the case of a lighter liquid to the actual free (volume) space in the column expressed as a fraction is termed the hold-up of the dispersed phase. Estimation of hold-up in packed liquid-liquid extraction columns is essential in predicting the performance of such columns for mass transfer operations.

Packed column gas-liquid hold-up has been studied in considerable detail[1-3]. However, until recently very few investigations[4-8] were reported for liquid-liquid systems and most of these were incidental to mass transfer studies in packed liquid-liquid extraction columns. Hold-up data in perforated plate and packed towers have been reported by Allerton and coworkers[9]. Minard and Johnson[10] while investigating flooding velocities in spray columns measured the hold-up data as well. Recently, Pratt and coworkers[11,12] measured the hold-up data below flooding and correlated the characteristic velocity as defined by them in terms of the physical properties of the liquid systems and packing characteristics. Venkataraman and Laddha[13] have reported considerable data on hold-up at flooding. Sitaramayya and Laddha[14] analysed the available data on hold-up in packed extraction

columns. In the present paper experimental data on hold-up below flooding are presented for a 3 in. tower. A generalized correlation has also been derived to estimate hold-up at flooding.

EXPERIMENTAL PROCEDURE

The extraction column used in the present investigation was a 3 ft long Pyrex glass tube having internal diam. of 3 in. and fitted with expanded end pieces having an internal diam. of $6\frac{1}{2}$ in. at the bottom and 6 in. at the top. The bottom end piece was made of a truncated cone mounted on a cylindrical end piece. The cylindrical portions of the end pieces were provided with sight glasses and with outlet and inlet connections. Both the ends of the glass column were fastened to the respective headers by means of flanges and Neoprene gaskets. The conical section at the bottom was also fitted with sight glass for observing column behaviour near the packing support and distributor. A distributor having holes of 1/16 in. diam. was used to disperse the lighter phase liquid at the bottom end of the tower. A schematic flow diagram of the experimental set-up is given in Fig. 1.

Feed flow of the continuous and discontinuous phases was motivated by means of constant air pressure provided by a 25 lb./sq. in. gauge air source. The high pressure air line was connected to the feed tanks through a pressure regulator to keep the pressure in the tanks constant. The column was filled with continuous phase and the rate adjusted to the desired value as observed by the manometer provided with the orifice. The manometer was calibrated directly for measurement of flow. The dispersed phase flow

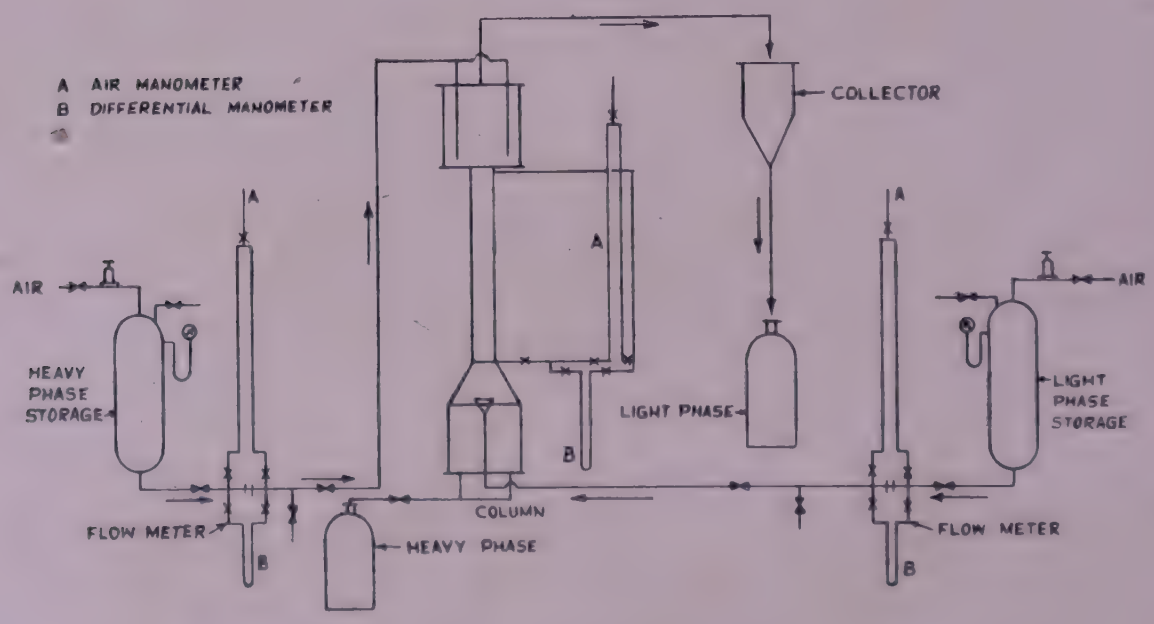

FIG. 1—EXPERIMENTAL SET-UP

was next turned on and brought to the desired rate, the interface position being stabilized in the middle of the separating section in the top header of the column by adjusting the outlet valve for the continuous phase going out of the column. Sufficient time was allowed for the column operation to reach a steady state. This was indicated when the interface at the top separating section became constant and the manometer readings across the orifice meter and the pressure drop readings across the column showed a steady position. The readings of the manometer for the flow of the continuous and discontinuous phases were then recorded. The exit phase flow rates were measured directly and checked with the inlet flow rates from the respective orifice meters. The following procedure was adopted for measuring the hold-up. When the column reached a steady state for any desired continuous and discontinuous phase flow rates, the inlet valves which allowed the phases to enter the column were closed simultaneously; the outlet valve for the continuous phase was also closed. It was then observed that the interface at the top descended slowly due to the accumulation of the dispersed phase held up in the column pushing down the continuous phase to the space occupied by it earlier. When no more movement of phases inside the column was observed, the continuous phase supply was turned on gradually and the discontinuous phase collected at the top was allowed to be displaced out of the column into a weighed receptacle. The continuous phase supply was cut out exactly when the interface at the top regained its original level. The weight of the dispersed phase received thus was determined and fractional hold-up of the dispersed phase in the free cross-section of the tower was calculated. Experimental data were recorded at various rates of discontinuous phase at constant values of the continuous phase flow rates in the column until any further increase of the discontinuous phase resulted in flooding the column. The approach of the flooding point could easily be judged by the rapid increase in the pressure drop across the packed section as recorded by the manometer. It was observed that at the flooding point a thin layer of the dispersed phase collected and tended to move below the packing support. This was found to be reproducible and therefore, the first appearance of the dispersed phase below the packing support was taken as the flooding point.

RESULTS AND CORRELATIONS

Fig. 2 shows a logarithmic plot of the fractional hold-up of the discontinuous phase (in column-free space) against the flow rates of the discontinuous phase. The parameter is the flow rate of the continuous phase. An examination of such a plot brings out a few interesting observations. Gayler and Pratt[11] have reported two or sometimes three, distinct regions (with one or two break points respectively) in such a plot. The first break was observed roundabout a hold-up of 0·15; and below a hold-up

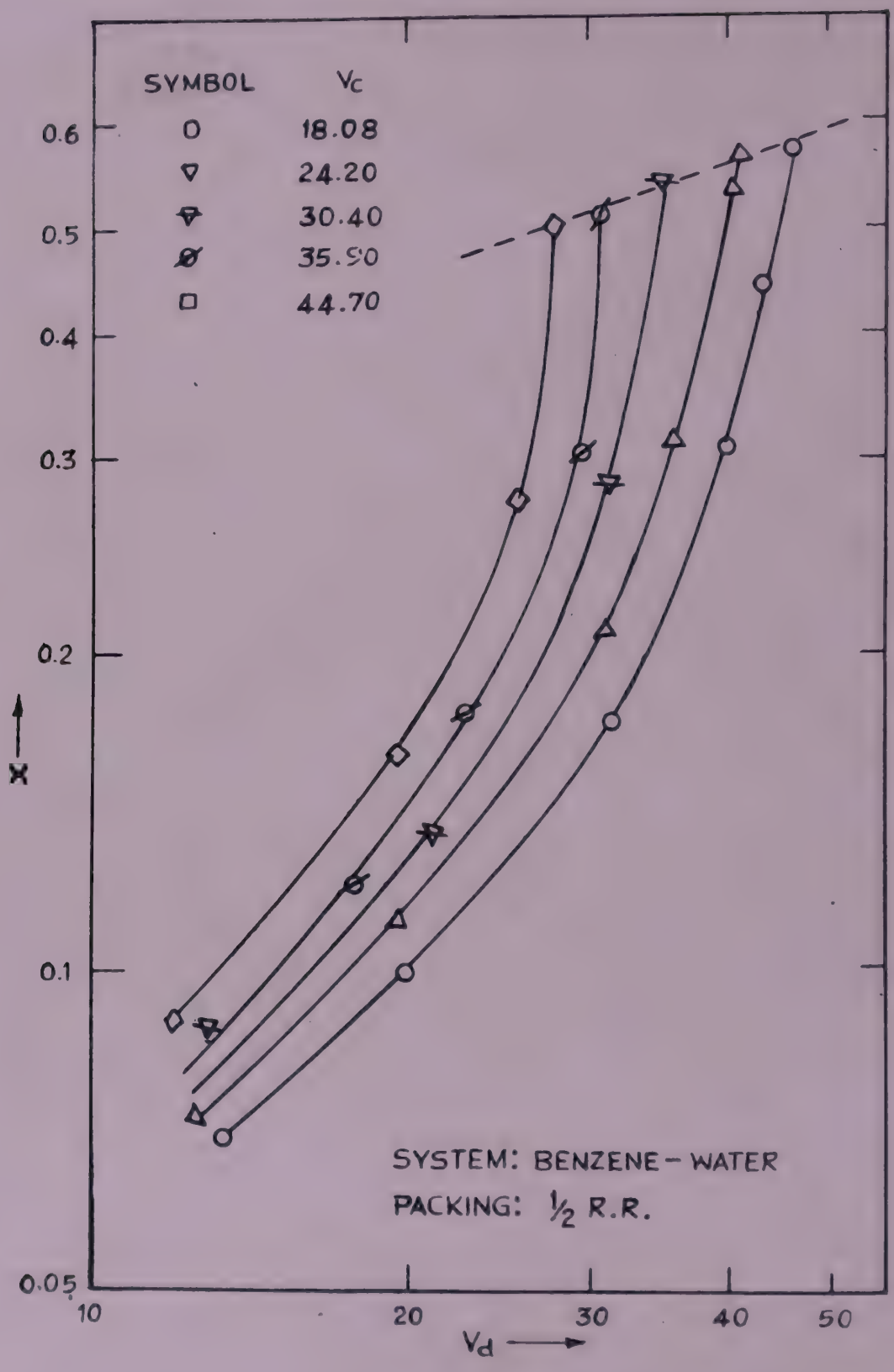

FIG. 2—PLOT OF HOLD-UP VERSUS DISPERSED PHASE VELOCITY

of 0·15, straight lines of slopes approximately equal to unity were obtained. This region was recognized by them as region of linear increases of hold-up and beyond this point the second region was identified as one of increasing hold-up. They also reported that in the case of systems of high interfacial tension a second break in the above curves would occur and the curve would then be almost parallel to the dispersed phase flow rate axis. This region was termed as one of constant hold-up. The data of the present investigation, however, show no such distinct regions but only smooth continuous curves. Similar observations have been made by Venkataraman[15] and Sitaramayya[16]. The performance characteristics of the countercurrent liquid-liquid extraction column involve many complex variables and as such clear-cut break points may not be warranted. Zenz[17] also suggests that by drawing logarithmic plots of hold-up smooth curves are obtained. It may also be observed that hold-up data below flooding can be represented by smooth curves in such plots for spray columns[10]. The dotted line in the figure shows flooding region.

Hold-up below Flooding. Gayler, Roberts and Pratt[12] correlated the mean rate of rise ν_r of the droplets of the discontinuous phase relative to the moving continuous phase by the following equation:

$$\nu_r = \frac{V_d}{ex} + \frac{V_c}{e(1-x)} = \bar{v}_o (1-x) \tag{1}$$

where $\bar{v}_o$ was defined by them as the limiting mean droplet velocity at zero continuous phase flow rate. They also indicated that the value of this characteristic velocity, $\bar{v}_o$ could be determined by plotting $\left(V_d + \frac{x}{1-x} V_c\right)$ versus $x(1-x)$ on Cartesian coordinates when straight lines of slope $m = e\nu_o$ would be obtained. Sitaramayya and Laddha[14] indicated that the following relationship by dimensional analysis of the problem:

$$m = C_1 \left[\frac{a}{e^3 g} \frac{\rho_c}{\triangle\rho}\right]^{-\frac{1}{2}}. \tag{2}$$

They analysed data on hold-up below flooding for a wide variety of liquid systems and tower diameters and proposed the following generalized correlation for estimation of hold-up below flooding:

$$\left[\frac{V_d}{V_c} + \frac{x}{1-x}\right] \left[\frac{V_c^2 a}{ge^3} \frac{\rho_c}{\triangle\rho}\right]^{\frac{1}{2}} = 0.683x(1-x). \tag{3}$$

The data of the present investigation for $\frac{1}{2}$ in. R.R. for the binary systems kerosene-water and benzene-water are plotted in Fig. 3. It is observed that the present data agree with the correlation proposed recently by

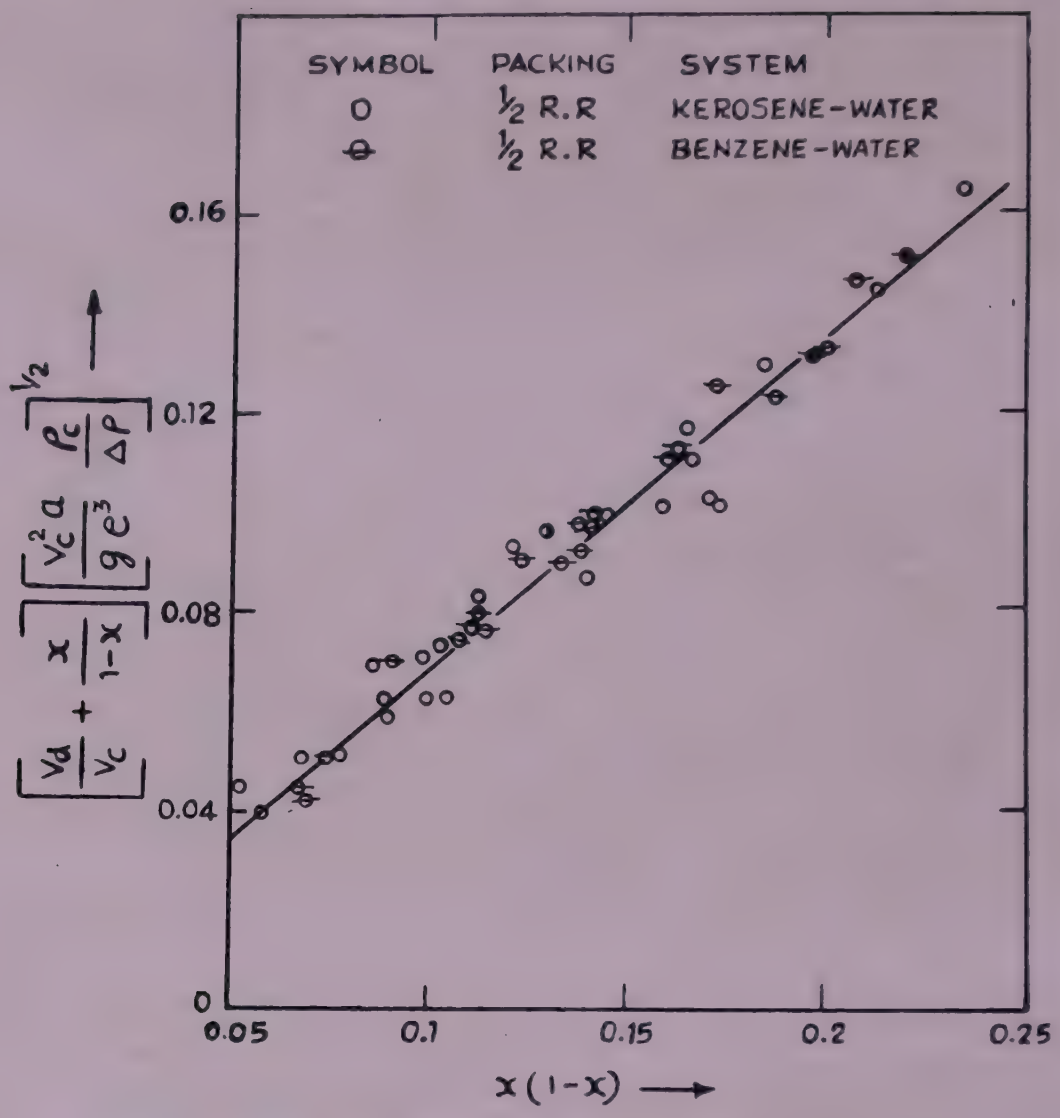

FIG. 3—GENERALIZED CORRELATION FOR HOLD-UP BELOW FLOODING

Sitaramayya and Laddha[14]. The following is the range of variables taken into account in the correlation:

Variable	*Range*
Ratio of the two viscosities	0·68—3·76
Ratio, $\rho_c/\triangle\rho$	2·9 —10·7
Interfacial tension, dynes/cm.	6·5 —41·8
Tower diameters, in.	2 —12
Tower packings	Raschig rings, Berl saddles and Lessing rings
Ratio of packing size to column diam.	1/24—1/6.

It may be observed that the effect of viscosity of both the phases and interfacial tension of the liquids appears to be negligible in the range of variables studied.

Hold-up at Flooding. The basic correlation representing the data for hold-up below flooding may be put in the following form:

$$\frac{V_d}{x}+\frac{V_c}{1-x}=m(1-x) \qquad (4)$$

where m has been shown to be proportional to $\left[\frac{a}{e^3 g}\frac{\rho_c}{\triangle\rho}\right]^{-\frac{1}{4}}$ as indicated earlier.

Differentiating at constant V_d,

$$-\frac{V_d}{x^2}+\frac{1}{(1-x)}\frac{dV_c}{dx}+\frac{V_c}{(1-x)^2}=-m \qquad (5)$$

and putting, $\frac{d\,V_c}{dx}=0$ at any constant value of V_d as the criterion of flooding, Equation (5) simplifies to

$$\frac{V_c}{(1-x)^2}-\frac{V_d}{x^2}=-m\,. \qquad (6)$$

Substituting the value of $\frac{V_c}{1-x}$ from Equation (4) in Equation (6) and simplifying,

$$V_d=2m\,x_f^2\,(1-x_f) \qquad (7)$$

where x_f is the value of x at flooding. Since m varies with $\left[\frac{a}{e^3\,g}\frac{\rho_c}{\triangle\,\rho}\right]^{-\frac{1}{2}}$, the above equation can be put in the following form:

$$x_f\sqrt{1-x_f}=C_2\left[\frac{V_d^3\,a}{g\,e^3}\frac{\rho_c}{\triangle\,\rho}\right]^n \qquad (8)$$

where n should have a value of 1/4. The data of Venkataraman[15] along with those of the present investigation for 3 in. tower for hold-up at flooding for the following systems and packings were analysed mathematically to determine the values of C_2 and n.

System	*Tower diam. in.*	*Packing*
MIBK-Water	2	$\frac{3}{8}$ in. R.R.; $\frac{3}{8}$ in. & $\frac{1}{4}$ in. L.R.
MIBK-10% glycerol	2	$\frac{3}{8}$ in. R.R.
MIBK-20% glycerol	2	$\frac{3}{8}$ in. R.R.
Kerosene-water	2	$\frac{3}{8}$ in.; $\frac{1}{4}$ in.; & $^3/_{16}$ in. L.R.
Kerosene-10% glycerol	2	$\frac{3}{8}$ in. R.R.
Benzene-water	3	$\frac{1}{2}$ in. R.R.

The data for Raschig rings for hold-up at flooding are plotted in Fig. 4 in terms of $x_f \sqrt{1-x_f}$ versus $\left[\frac{V_d^2}{g\epsilon^3}\frac{a}{}\frac{\rho_c}{\triangle\rho}\right]$ on logarithmic coordinates. Fig. 5 shows such a plot for Lessing rings. Mathematical analysis of the data by the method of least squares indicates that the values of C_2 and n for Raschig rings are 0·5195 and 0·0828 respectively, while for Lessing rings these values are 0·3512 and 0·0778. It will be observed that the value of n is very nearly the same in both cases, but it is much smaller than 1/4 as predicted in the correlation. Since the value of n is very small, it appears that the product $x_f \sqrt{1-x_f}$ is very nearly constant at flooding.

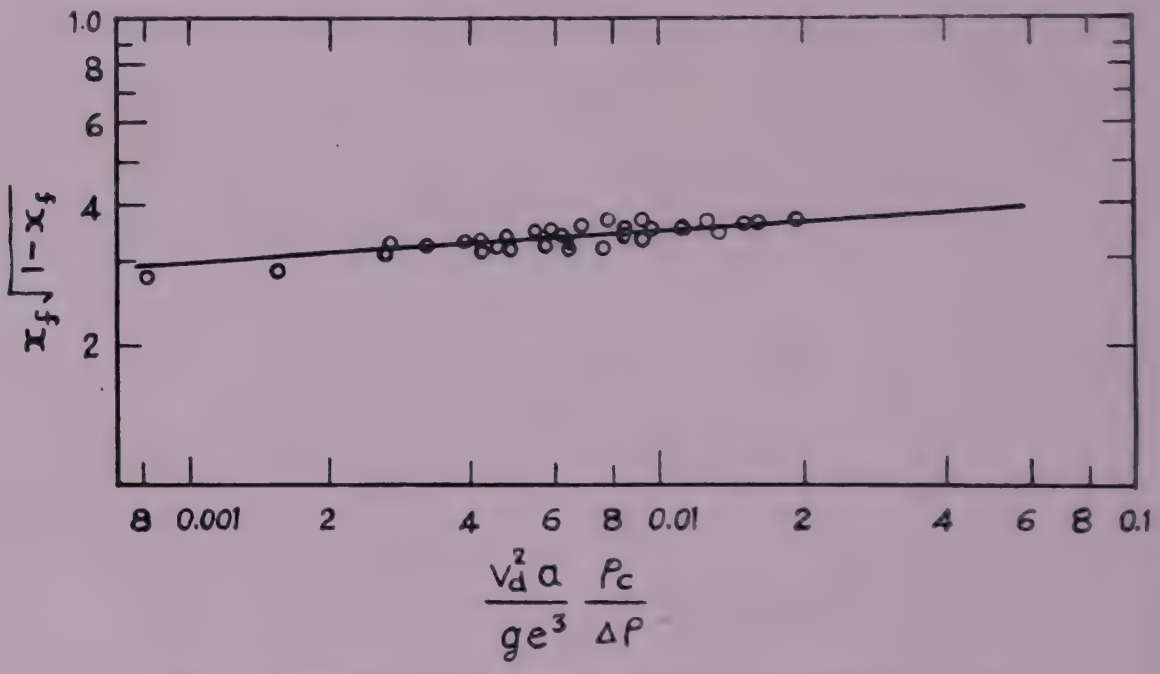

FIG. 4—CORRELATION OF HOLD-UP AT FLOODING WITH RASCHIG RINGS

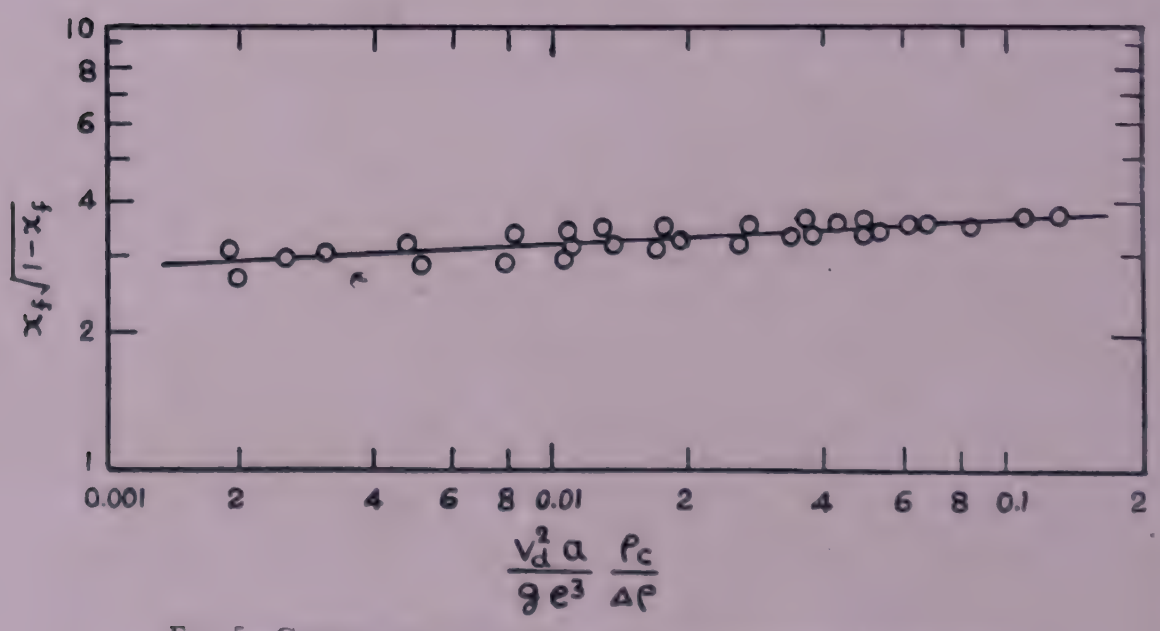

FIG. 5—CORRELATION OF HOLD-UP AT FLOODING WITH LESSING RINGS

Nomenclature

a = Superficial area of packing, ft^{-1}
C_1 and C_2 = Constants
e = Fractional voids in packed tower
g = Gravitational acceleration, ft/hr^2
v_r = Rate of rise of droplets of discontinuous phase, ft/hr
v_0 = Characteristic velocity, ft/hr
V_c = Superficial velocity of continuous phase (empty tower cross-section), ft/hr
V_d = Superficial velocity of discontinuous phase (empty tower cross-section), ft/hr
x = Fractional hold-up of dispersed phase in column-free space
x_f = Hold-up at flooding
ρ_c = Density of continuous phase, lb./cu. ft
ρ_d = Density of discontinuous phase, lb./cu. ft
$\triangle\rho$ = Density difference, lb./cu. ft

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Application of Corrosion-resistant Nickel, Nickel Alloys and Stainless Steels in Chemical Industry

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The use of nickel, certain high-nickel alloys and austenitic chromium-nickel stainless steels as materials of construction in chemical plants to stand against various corrosive reactants is discussed. The effect of various factors affecting corrosion of stainless steels and preferred practice in construction and use of stainless steel equipment from the corrosion point of view are enumerated.

The chemical industry differs from other industries in the multiplicity of the materials used for the construction of its plant and equipment. For example, in the mechanical industry, iron or steel and in the electrical industry, copper, play such a dominant part that the other materials used can be regarded as of secondary importance. But in the chemical industry no single material dominates the field for plant construction. Owing to a variety of requirements, the entire range of metals and non-metals finds application.

Every material will corrode in certain environments and will display a noticeable resistance to corrosion in others. The task of the chemical plant designer faced with corrosion problems is to choose the material which will resist the particular set of conditions to be encountered. But corrosion resistance is not the only attribute to be considered. Cost must always influence the choice of a material and so must fitness for normal fabrication operations such as forming and welding. Good mechanical strength is also necessary, good heat conductivity is often desirable, and it must be producible in the forms in which the plant constructor needs. Before a final choice is made, the factors that affect corrosion—concentration, temperature, aeration, rate of flow, influence of other metals in the same plant—must all be considered. These and other factors make the selection of a corrosion-resisting material anything but a simple matter. Even then, a test under actual operating conditions is desirable.

This paper will be mainly concerned with the use of nickel, certain highnickel alloys and the austenitic chromium-nickel stainless steels, which are among the established materials of construction for chemical

plants. In view of the rapid growth of the Indian chemical industry in recent years and the stress laid on indigenous design and fabrication of plant, the information given in this paper should help chemical engineers in the proper choice of corrosion-resisting materials for various items of chemical plant. There is unfortunately a tendency in this country to use the cheapest material available, the choice in most cases falling on mild steel. This is a very great mistake as one must remember that freedom from repairs and from contamination of the reactants often makes an expensive material the most economical in the long run.

NICKEL AND HIGH NICKEL ALLOYS

The ability of nickel to resist corrosion has long been recognized and it is an important constituent of many of the corrosion-resisting materials which have been developed and used widely for chemical plant construction.

NICKEL

This metal is a relatively noble element; in the electromotive series it is shown to be 0·21 V. more noble than iron. The practical significance of this is that nickel does not readily displace hydrogen from any of the common acids with which it may be used, and a supply of some oxidizing agent, such as dissolved air, is necessary to enable corrosion to proceed. It is important to remember that oxidizing conditions accelerate the corrosion of nickel, and reducing conditions retard attack.

However, nickel acquires protection against certain forms of attack by the development of a corrosion-resisting or passive oxide film; mildly oxidizing conditions do not therefore always accelerate corrosion, but care should always be exercised before using nickel under such conditions.

The behaviour of nickel in contact with some of the commoner corrosive media is indicated below:

Fresh Water. Corrosion rates are low in both distilled and natural waters. Highly resistant to natural waters containing hydrogen sulphide and carbon dioxide.

Salt Water. Although nickel has good resistance to agitated or flowing sea water, it may suffer pitting or local attack in stagnant conditions. For this reason Monel is generally preferred.

Neutral and Alkaline Salts. Good resistance to neutral and alkaline salts such as chlorides, carbonates, sulphates, nitrates and acetates.

Acid Salts. Useful resistance especially to such acid chlorides as those of ammonia and zinc.

Oxidizing Acid Salts. Usually appreciably corrosive to nickel.

Oxidizing Alkaline Salts. May be very corrosive to nickel. Nickel is not, however, affected by the alkaline solution containing hydrogen peroxide used for textile bleaching.

Mineral Acids: *Sulphuric Acid.* Though generally inferior to Monel and lead, its resistance is adequate for certain uses. The use of nickel with chamber sulphuric acid is to be avoided.

Hydrochloric Acid. Nickel has useful resistance. Concentration, temperature and aeration have a considerable effect.

Organic Acids and Compounds. Nickel has a good resistance to fatty acids and phenol.

Alkalies. Excellent resistance to caustic soda at all temperatures and concentrations.

Nickel can be fabricated by hot or cold working without presenting any unusual difficulties. It can be joined by all commercial methods, including brazing, gas, arc and resistance welding.

NICKEL ALLOYS

The resistance of nickel-containing alloys to fluorine and hydrofluoric acid has led to their adoption in many of the processes concerned with the fluorination of uranium compounds for atomic energy purposes. The nickel-copper alloy has been most widely used in such applications, but for high-temperature reactions the nickel-chromium-iron alloy has been selected.

The nominal composition of nickel alloys is given in Table 1. Table 2 gives the uses of nickel and nickel alloys in electrolytic caustic soda equipment.

TABLE 1—NOMINAL COMPOSITION OF NICKEL AND HIGH NICKEL ALLOYS

	Nickel alloy	Monel	'K' Monel	Cast Monel	Inconel	Ni-o-nel	Corronel 210
Nickel	99*	63*	66	63-68	72*	40	66
Copper	0·25†	28-34	29	Bal.	0·7†	1·75	—
Iron	0·40†	2·50†	0·90	3·0†	6·10	31	6
Manganese	0·35†	2·00†	0·40	0·5-1·5	1·0†	0·60	—
Silicon	0·15†	0·50†	0·25	0·5-1·2	0·5†	0·40	—
Carbon	0·15†	0·30†	0·15	0·30	0·2†	0·05	—
Sulphur	0·01†	—	0·005	—	0·03†	—	—
Magnesium	0·20†	—	—	—	—	—	—
Chromium	—	—	—	—	14-17	21	—
Molybdenum	—	—	—	—	—	3·0	28
Other elements	—	S, 0·02† Al, 0·5	S, 1·0† Al, 2·75	0·5 including Mg, 0·08-0·12; Pb, nil	—	Bal. trace elements including Ti	—

*min.; †max.

TABLE 2 –USE OF NICKEL AND NICKEL ALLOYS IN MAKING ELECTROLYTIC CAUSTIC SODA EQUIPMENT

Equipment	Material(s)
Brine pumps	Monel
Brine heaters	Nickel and Monel
Evaporators:	
Bodies	Nickel-clad steel or lined with nickel sheet
Steam chests	Nickel or Monel tube sheets Nickel, Monel or nickel-clad steel downtakes Nickel or Monel tubes
Coils	Nickel or Monel
Screens	Monel or nickel
Catchalls	Nickel-clad steel or lined with nickel sheet
Heat exchangers	Nickel or Monel
Pumps:	
Bodies Shafts Impellers	Nickel or Monel
Valves and fittings	Nickel or Monel
Pipe lines	Nickel or Monel
Filters:	
Bodies and drums	Nickel or nickel-clad steel
Filter cloth Backing wire Winding wire	Monel or nickel
Piping, valves and fittings	Nickel or Monel
Settling tanks	Nickel-clad steel or lined with nickel sheet
Storage tanks	Nickel-clad steel or lined with nickel sheet
Crystallizers:	
Bodies	Nickel-clad steel or lined with nickel sheet
Shafts and agitators	Nickel or Monel
Centrifugals	Monel baskets and wire cloth liners
Tank cars:	
Bodies	Nickel-clad steel
Coils	Nickel
Caustic pots	Low-carbon nickel-clad steel or Inconel-clad steel

Use Monel up to 50 per cent caustic soda, 'AT' Nickel in the range 50–75 per cent and low carbon 'AT' Nickel at higher concentrations.

Ni-Cu Alloy (Monel)

This alloy was one of the earliest alloys to be generally accepted for corrosion resistance, and has been in commercial use for over fifty years.

The position which Monel occupies today is due more to a combination of properties than to any one property. It resists attack by a great variety of corrosive media. It is strong and tough, and retains its strength to a very useful degree at both elevated and sub-zero temperatures. It can be readily fabricated and joined by the usual methods. It is available in all the accepted commercial forms, including castings. It is, in fact, a general purpose corrosion-resisting alloy capable of giving good service in conditions of a widely varying nature.

Monel is more resistant than nickel under reducing conditions and more resistant than copper under oxidizing conditions. The net result is that it is generally more resistant than either of its principal constituents. The behaviour of Monel towards some of the more common corrosive media is indicated below:

Fresh Water. Excellent resistance to corrosion by waters of all kinds.

Salt Water. Excellent resistance to sea water and to concentrated salt solutions at all temperatures.

Neutral and Alkaline Salts. Corrosion rate negligible.

Acid Salts. Useful resistance to acid salt solutions such as zinc chloride, ammonium sulphate, ammonium chloride.

Oxidizing Acid Salts. Monel is not highly resistant.

Oxidizing Alkaline Salts. Hypochlorites are the only common alkaline salts that are definitely corrosive to Monel.

Mineral Acids. Good resistance to all acids except those of a highly oxidizing character. In non-oxidizing acids, dissolved air or other oxidizing agents increase the corrosion rate. Monel shows a very low rate of corrosion in contact with hydrofluoric acid over a wide range of temperatures and concentrations.

Organic Acids and Compounds. Useful resistance to all the common organic acids, and practically free from corrosion by neutral and alkaline organic compounds.

Alkalies. Almost completely resistant to most alkaline solutions.

Ni-Cr-Fe Alloy (Inconel)

Like other alloys in the nickel-chromium-iron group, Inconel has great strength and oxidation resistance at high temperatures and it is therefore often selected for furnace parts and similar equipment. It is also resistant to many corrosive products and some indication of its suitability is given here.

Where austenitic steel has failed due to stress-corrosion cracking, Inconel can be considered a first alternative due to its superior resistance to this type of attack.

Neutral and Alkaline Salts. Unaffected by most of them.

Oxidizing Acid Salts. Inconel is superior to nickel and Monel in its resistance to oxidizing acid salts, although this resistance does not extend to solutions containing appreciable percentages of salts like ferric chloride, cupric chloride and mercuric chloride.

Mineral Acids. Although it has a fair resistance to sulphuric and hydrochloric acids, other materials as indicated elsewhere in this article would normally be chosen.

Oxidizing Acids. Highly resistant to strongly oxidizing acids at atmospheric temperature. There are, however, many other materials which are more economical for such applications; Inconel is used only when other considerations make it necessary.

Organic Acids and Compounds. Exceptionally resistant to hot fatty acids.

Alkalies. Practically free from corrosion by alkaline solutions. Useful also in resisting corrosion by alkaline sulphur solutions.

Wet and dry Gases. Not affected by any dry gas at atmospheric temperatures. Useful for handling hydrogen chloride and chlorine at high temperatures. Resistant to ammonia, nitrogen and hydrogen at high temperatures.

Mechanical Properties. Inconel has a high strength particularly after severe cold working. It has also good strength properties at high temperatures.

It can be fabricated by the usual processes without undue difficulty. It has good ductility and is suitable for deep drawing operations.

Ni-Mo-Fe Alloy (Corronel 210 and 220)

Corronel 210, formerly known as Corronel B, has been in production for some years. It was developed mainly to resist the attack by three of the most important mineral acids—hydrochloric, sulphuric and phosphoric, in conditions too severe for other commercial alloys.

Heat treatment is usually necessary after welding Corronel 210 to ensure satisfactory resistance to attack. Without this heat treatment fabrications in Corronel 210 may suffer premature failure adjacent to the welds when exposed to acids and acid salts.

To obviate the difficulty and expense of carrying out heat treatment a new grade of the alloy known as Corronel 220 has now been introduced. Corronel 220 which contains a small amount of vanadium is not normally susceptible to weld decay and post-welding heat treatment is not necessary for this alloy. Corronel 220 possesses about twice the corrosion resistance of Corronel 210 under similar conditions.

An indication of the resistance of the Corronel alloys is given below:

Hydrochloric Acid. Highly resistant at all concentrations and temperatures. These alloys are also resistant to moist hydrogen chloride.

Under reducing conditions, Corronel alloys may be regarded as the most satisfactory alloys commercially available for handling hydrochloric acid. The presence of oxidizing salts, however, considerably increases the corrosion rate.

Sulphuric Acid. Adequate resistance to all concentrations up to 100°C. It also resists boiling acid in concentra ions up to 60 per cent. Even in 96 per cent acid at 150°C. it can give useful service. As with hydrochloric acid the presence of oxidizing salts considerably increases the corrosion rate.

Phosphoric Acid. Excellent resistant even at temperatures approaching boiling point of concentrated acid.

Other corrosive Media. Corronel alloys are extremely resistant to many other corrosive substances, such as organic acids, calcium chloride, brines, etc. and can be employed in plant where attack has been found severe. In general, however, other materials can take care of less severe corrosive conditions.

Mechanical Properties. Corronel alloys have high strength and hardness. Simple forming operations can be carried out in the cold condition, more power being required than for the equivalent operation on the same thickness of mild steel. More severe forming operations are generally performed in the hot condition.

Corronel alloys can be welded by the usual methods, and as already stated, post-welding heat treatment is necessary for Corronel 210 to ensure full resistance to severe attack.

Ni-Cr-Fe-Mo Alloy (Ni-o-nel)

This alloy has also been developed to meet corrosive conditions of unusual severity. In contrast to nickel and Monel, Ni-o-nel is at its best when oxygen or oxidizing agents are present. In the annealed conditions, this alloy can be cold bent. Hot forming should be followed by rapid air cooling or a water quench. Welding can be undertaken by the metallic arc or inert gas-arc methods.

Ni-o-nel is suitable for handling hot sulphuric acid solutions, whether oxidizing agents are present or not. Due to the presence of a chromium oxide film on the surface it does not readily release hydrogen from acid solutions. It is for this reason that oxidizing conditions are generally beneficial. The presence of reducing agents may tend to break this passive film down, although to a lesser extent than with stainless steels.

Corrosion rates are subject to considerable variations depending on the process conditions. The following notes will, however, give an indication of the conditions in which Ni-o-nel is useful.

Sulphuric Acid. Suitable for hot acid solutions, whether oxidizing agents are present or not, in conditions where stainless steels and Monel are unsatisfactory. Excellent resistance to all concentrations at room temperature.

TABLE 3—CORROSION TESTS OF NICKEL ALLOYS IN BOILING PHOSPHORIC ACID (85%)

	Corrosion rates*, *in./year*			
	Period 1	Period 2	Period 3	Av.
Corronel B	0·004	0·005	0·003	0·004
Ni-o-nel	0·036	0·035	0·034	0·035
Hastelloy C	0·114	0·156	0·130	0·133
Stainless steel (18/8/3 Type)	0·427	0·432	0·477	0·445

*Corrosion rates were determined in three 24-hr test periods.

Useful resistance up to about 70 per cent concentration at 80°C. and up to 40 per cent concentration at boiling point. It is suitable for use with mixtures of sulphuric acid with nitric acid, cupric sulphate or ferric sulphate.

Sulphurous Acid. Useful resistance to hot acid solutions.

Phosphoric Acid. Useful resistance even in boiling concentrated solutions, although not as good as Corronel alloys (Table 3).

Nitric Acid. Resistance to many nitric acid solutions over a wide temperature range. In view of the resistance of stainless steels, the application of Ni-o-nel is likely to be with mixtures of nitric and other acids, such as nitric-sulphuric, nitric-phosphoric, and some nitric-hydrofluoric solutions.

Organic Acids. Highly resistant to most organic acids; excellent resistance to boiling concentrated acetic acid as well as acetic-formic acid mixtures, maleic, phthalic acids and a number of others which are frequently corrosive to stainless steel.

Sea Water and Chlorides. Ni-o-nel is resistant to certain troublesome cooling waters. This is important in heat exchange equipment (handling chemical corrosives) which employs sea water for the cooling media. Ni-o-nel gives good resistance to pitting and stress-corrosion cracking but care should be exercised when it is used with oxidizing chlorides such as ferric or cupric chloride.

AUSTENITIC STAINLESS STEELS

Before considering the attributes of the other nickel alloys it will be convenient to discuss the austenitic chromium-nickel stainless steels. As is well known, the chemical industry is one of the most important users of the austenitic stainless steels, but the materials also find many applications in the food, dairy and brewing industries. Other significant outlets are in the aircraft, automotive and domestic fields. To meet all these needs many varieties have been developed; no fewer than 37 grades are listed by the American Iron and Steel Institute. This number includes ferritic and

TABLE 4—STANDARD TYPES OF AUSTENITIC STAINLESS STEELS

AISI Type No.	Composition, %						Remarks
	Chromium	Nickel	Carbon (max.)	Manganese (max.)	Silicon (max.)	Others	
201	16-18	3·5-5·5	0·15	5·5-7·5	1	N 0·25 max.	Low-nickel equivalent of Type 301
202	17-19	4-6	0·15	7·5-10	1	N 0·25 max.	Low-nickel equivalent of Type 302
301	16-18	6-8	0·15	2	1		High work-hardening
302	17-19	8-10	0·15	2	1		General purpose "18/8"
302B	17-19	8-10	0·15	2	2-3		More scaling resistance than Type 302
303	17-19	8-10	0·15	2	1	0·6 Mo or 0·6 Zr optional	Free machining "18/8"—heavy cuts
303Se	17-19	8-10	0·15	2	1	Se 0·15 min.	Free machining "18/8"—light cuts
304	18-20	8-12	0·08	2	1		Low-carbon—for welding
304L	18-20	8-12	0·03	2	1		Low-carbon—for welding
305	17-19	10-13	0·12	2	1		Lower work-hardening rate
308	19-21	10-12	0·08	2	1		Welding rod—for ductility
309	22-24	12-15	0·20	2	1		High-temperature strength and scaling resistance
309S	22-24	12-15	0·08	2	1		Low-carbon Type 309—for welding
310	24-26	19-22	0·25	2	1·5		Better high-temperature strength and scaling resistance
310S	24-26	19-22	0·08	2	1·5		Low-carbon Type 310—for welding
314	23-26	19-22	0·25	2	1·5-3		Most scaling resistant
316	16-18	10-14	0·08	2	1	Mo 2-3	Increased corrosion resistance
316L	16-18	10-14	0·03	2	1	Mo 2-3	Low-carbon Type 316—for welding
317	18-20	11-15	0·08	2	1	Mo 3-4	More corrosion resistant than Type 316
321	17-19	9-12	0·08	2	1	Ti 5 × C min.	Stabilized against carbide precipitation
347	17-19	9-13	0·08	2	1	Cb + Ta 10 × C min.	Stabilized against carbide precipitation
348	17-19	9-13	0·08	2	1	Cb + Ta 10 × C min. but Ta 0·1 max.	Stabilized against carbide precipitation

martensitic grades but 22 of the 37 are chromium-nickel types. The nominal compositions of the standard types of austenitic stainless steels are given in Table 4.

As with other materials, various factors govern the choice of a chromium-nickel austenitic steel for a particular application, e.g. corrosion-resistance, structural stability or strength at elevated temperature, easy fabrication. These attributes are necessarily balanced against economic aspects, such as expected service life and degree of maintenance required, not forgetting the ubiquitous factors of price and delivery. Much has already been written about the properties and applications of stainless steels but it may be useful to examine here the main factors affecting the corrosion of these steels and to give some practical guidance to the chemical plant designer and fabricator.

Factors affecting Corrosion of Stainless Steels

Effect of Thermal Exposure. When heated for an appreciable length of time between 425°C. and 900°C. the austenitic structure of some stainless steels may undergo a change which renders them susceptible to intergranular corrosion upon exposure to a number of corrodents. After such an attack the steels may appear perfectly sound, but upon more detailed examination they may be found to possess very little strength. Welding operations on the straight chromium-nickel austenitic steels may also leave an area adjacent to the welds in this sensitive condition. Additions of titanium in amounts of four to six times the carbon content and niobium eight to sixteen times the carbon content greatly inhibit the changes associated with susceptibility to intergranular corrosion.

Crevice Corrosion. In the design of stainless steel equipment, all shapes and joints which form crevices or deep recesses should be avoided, for otherwise oxygen does not have ready access to the remote areas in the crevices and these may become appreciably anodic to the remaining exposed and aerated areas of the equipment. Corrosion therefore progresses in the crevices and in some instances may become severe.

Galvanic Couples. When designing equipment to be constructed with several materials, thought must be given to the possible galvanic couples. The stainless steels are usually quite cathodic relative to other alloys but their potentials may vary over a wide range depending upon whether they are in an active or passive state. Type 304 stainless steel in sea water exhibits electrode potentials from +0·5 to −0·28V. referred to standard calomel electrode. The austenitic stainless steels accordingly may be expected to be cathodic to most of the structural alloys, such as mild steel and aluminium, and hence will benefit from cathodic protection.

Influence of Elements other than Nickel and Chromium

Carbon. Increasing carbon content tends to increase the susceptibility of stainless steels to intergranular attack. Holding the carbon content to a

maximum of 0·03 per cent is sufficient to avoid sensitization during welding and stress-relief annealing.

Silicon, Manganese and Nitrogen. Silicon in stainless steels above that required for deoxidation slightly reduces their resistance to corrosion by nitric acid. Manganese has no effect on their resistance to nitric acid. Nitrogen content also makes no difference to corrosion rates.

Molybdenum. Pitting corrosion, which is most frequently developed by chloride solutions, is rendered less severe by the addition of 2 to 3 per cent of molybdenum to stainless steels. Molybdenum additions also have the specific effect of reducing corrosion of the stainless steels in certain media such as sulphurous acid, sulphuric acid, phosphoric acid, formic acid and some hot organic acids.

Copper. The addition of copper to austenitic stainless steels of higher alloy content greatly improves their resistance to corrosion by sulphuric acid. As a result, a number of copper-bearing stainless steels have solved industrial problems involving the handling of sulphuric acid at concentrations and at temperatures at which the simple chromium-nickel stainless steels cease to be useful or economical.

STAINLESS STEEL EQUIPMENT DESIGN

Preferred practice in the construction and use of stainless steel equipment from the corrosion standpoint may be summarized as follow:

(1) Choose the proper alloy for the service. Severe corrosive conditions may require the molybdenum alloys, AISI Types 316 or 317, the more highly alloyed Type 310, or the more complex proprietary alloys containing molybdenum plus extra amounts of nickel or chromium, or both.

(2) Where heating, that might result in sensitization is anticipated, as in welding or stress relief annealing, avoid this effect by the use of stabilized or extra low carbon compositions, or, as a less desirable step, provide appropriate subsequent heat treatment to eliminate such sensitization.

(3) Avoid crevices and sharp corners or recesses which may become the seats of destructive corrosion.

(4) Where possible, provide good aeration and agitation of corrosive media to avoid the accumulation of deposits on the metal surfaces. The smoother the finish, the easier it will be to avoid or remove such deposits.

(5) Overcome the influence of activating chemicals such as chlorides, in closed circulating systems by the addition of oxidizing inhibitors, such as chromates or nitrates.

(6) Avoid locked-in tensile stresses associated with fabrication or eliminate them by stress relief annealing, especially if the corrosive medium is one that can cause stress corrosion cracking.

(7) Provide clean smooth surfaces and keep them clean. Remove scale with nitric acid. Remove carbon deposits mechanically rather than by

burning which may cause carbon pick-up and subsequent sensitization. Do not use ordinary steel wool since it will contaminate and mar the surface with rusty iron particles. Stainless steel wool is satisfactory for removing heavy deposits.

NICKEL-CLAD STEELS

Whatever merits a metal may have as a corrosion material, its applications are restricted, if it is available in only limited forms. Very often it is necessary to use nickel, nickel alloy or stainless steel in such thickness as would make the cost prohibitive. In such circumstances it may be possible to employ clad steels or some form of vessel lining. Usually the backing material is mild steel although occasionally low-alloy steels are employed in order to obtain added strength. The value of such cladding or lining obviously depends upon the possibility of maintaining continuity of the corrosion-resisting materials. This can be achieved by the use of special welding techniques, which have been described in literature.

For some purpose, advantage can be taken of the properties of nickel in the electrodeposited form: such coatings have given satisfactory service on equipment where lack of protection by the coating would have resulted in the contamination or discolouration of the produce due to corrosion of the basis metal by the aggressive corrosive media involved. Deposition of nickel by non-electrolytic processes has also been developed, notably the Kanigen method. No anodes are required, and elaborate racking procedure for suspending the article in the plating solution is unnecessary. During immersion the whole of the surface becomes coated with an alloy containing about 7 per cent phosphorus, and the thickness of the deposit is uniform irrespective of the complexity of the shape of the article; indeed, the most important attribute of this system of plating is its ability to deposit uniform thicknesses over any shape of surface. Another non-electrolytic method is the Niphos process, by which a mixture of nickelous oxide and dibasic ammonium phosphate is applied to the article as a slurry. The coated part is dried and fired, after which the nickel deposit is found to contain about 5 per cent phosphorus. Some diffusion of the coating into the steel takes place and consequently adhesion is normally very good. Indications are that in marine or industrial atmospheres the corrosion-resistance of steel parts plated with Niphos coatings is not so good as that of deposits made by electrolytic methods or by the chemical reduction process.

For many years the rayon industry has demanded caustic soda of very low iron content, and nickel and nickel-clad steels have, therefore, been widely used in caustic soda manufacturing plants, handling and transport of caustic soda of that grade in road and rail tankers. An unusual example of this application was the use of nickel-clad steel for the holds for the S.S. 'Dow-Chem' which regularly transports high-grade caustic soda. This behaviour

of nickel in highly concentrated caustic soda or fused alkali is due to the protective nature of the oxide film which forms on the surface of the metal. The film is thin and black and in its presence the rate of corrosion by fused caustic soda is of the order of only 0·003 in./year. Temperatures of about 320°C. favour the development of this protective oxide, although at lower temperatures (around 200°C.) a non-protective greenish form of the oxide may develop. For applications in molten caustic soda at temperatures above 320°C. a special grade of low-carbon nickel is necessary because of its greater resistance to intergranular attack by the alkali. The susceptibility of nickel to sulphur attack is well known and the presence of sulphur in the alkali will lead to intergranular attack at high temperatures. The presence of chlorates will also accelerate corrosion of nickel plant handling the fused caustic alkalis.

MATERIALS RESISTANT TO INORGANIC ACIDS

Hydrochloric Acid. The nickel-molybdenum-base alloys (Table 1) may be regarded as extending the corrosion resistance of nickel-base materials to an even wider range of concentrations and temperatures. Hydrochloric acid is perhaps the most corrosive of the common acids, it will destory protective oxide films, and since chlorides are appreciably soluble there is little possibility of providing a resistant coating. Only a noble material, one which does not release hydrogen from the acid, is likely to offer useful resistance to attack. Copper might be successful but for the fact that the nobility is reduced by the tendency to form complex cupric chloride ions and by the marked acceleration of attack in the presence of oxygen or oxidizing agents. Nickel itself possesses a useful resistance to the acid, but the value of copper in improving the nobility of nickel is seen in the resistance of the nickel-copper alloy to hydrochloric acids in moderate concentrations and under non-oxidizing conditions.

Molybdenum has a marked effect on the nobility of nickel and its resistance to hydrochloric acid. Most of the commercial alloys based on the nickel-molybdenum system contain 26–30 per cent of molybdenum, usually with about 5 per cent of iron derived from the ferro-molybdenum used in making the alloy. These are the alloys often employed where resistance to hot and concentrated solutions of hydrochloric acid is required. The presence of cupric and ferric salts, however, accelerates the rate of attack by hydrochloric acid. The nickel-molybdenum alloys have also a good resistance to attack by sulphuric and phosphoric acids.

Nitric Acid. It is well known that stainless steel is a great boon to the nitric acid industry whose development on its present scale would hardly have been possible without this material. The stabilized steels of the 18/8 chromium-nickel type have been used extensively for welded plant but cases of failure have occurred in nitric acid service due to localized pene-

tration in the weld area, in the form of 'grooving', attack corrosion and 'knife-line' corrosion. Investigation of the problem has shown the shortcomings of the 18/8 Ti steel in nitric acid concentrations above 50 per cent at elevated temperatures. In these circumstances the use of niobium-stabilized stainless steel is to be preferred, but even this steel, although less sensitive to the heat of welding, is not completely immune from intergranular attack in boiling 70 per cent (by weight) nitric acid.

Sulphuric Acid. Probably the corrosive agent most commonly employed in chemical processes is sulphuric acid. Perhaps for no corrosive medium is there available such a choice of materials which are of at least some use in handling the acid within certain limiting concentrations and ranges of temperature. Cold concentrated sulphuric acid can be handled in mild steel. Over a more general range the value of lead is well known, but its mechanical strength introduces complications when designing a chemical plant. Conditions involving extremely high concentrations and temperatures may be met by the use of some expensive materials such as tantalum, but iron-silicon and nickel-silicon alloys are useful, the latter having been used for the concentration of sulphuric acid by evaporation. Unfortunately, these silicon alloys are available only in the cast form, and require careful handling during fabrication.

Experience has shown that nickel-copper alloys have a useful field of service in plant for the processing of non-oxidizing materials involving sulphuric acid under substantially air-free conditions as shown in Table 5. The corrosion rate, however, rises rapidly with any increase in the oxidizing characteristics of the reactants, and free access of air can render the corrosion resistance of nickel-copper alloys inadequate for useful service. At high temperatures and concentrations sulphuric acid becomes strongly oxidizing

TABLE 5—CORROSION IN BOILING SULPHURIC ACID SOLUTIONS

(*No aeration and agitation except boiling*)

Material	Average corrosion rate (*in./year*) with					
	5% acid at 102°C.	10% acid at 103°C.	19% acid at 105°C.	50% acid at 123°C.	75% acid at 182°C.	96% acid at 293°C.
Monel ..	0·0034	0·0024	0·0075	0·65	2·3	3·3
Nickel ..	0·034	0·12	0·11	3·4	0·91	2·3
Inconel ..	0·24	0·39	0·64	7·8*	4·8*	0·86
Chemical lead ..	0·016	0·015	0·042	1·2	†	‡
Antimony lead ..	0·016	0·019	0·046	0·023	0·57	‡
Tellurium lead ..	0·025	0·021	0·035	0·023	0·092	36·3

*Test period 4 hr; †Specimens dissolved in ¾ hr; ‡Extremely rapid attack

in character, and to meet such conditions it is necessary to employ nickel alloys containing chromium. A nickel-chromium-iron alloy, such as Ni-o-nel, containing small proportions of molybdenum and copper has recently been developed to cover the field of intermediate acid concentrations under oxidizing conditions at temperatures at which the nickel-copper alloys cannot be employed. This alloy is resistant to weld-decay in the environments for which it is likely to be selected although it shows some sensitivity when treated with boiling 65 per cent nitric acid. For severe service conditions for which a more expensive material is justified the nickel-molybdenum alloys are particularly useful. Under non-oxidizing conditions, such alloys are more resistant to corrosion by sulphuric acid than any other wrought material; they have been chosen for valves, heating coils, steam injectors and similar components required to handle sulphuric acid at concentrations of 20–100 per cent and at temperatures of 50–120°C.—conditions under which cheaper materials undergo corrosion so rapidly as to render them of no practical value. These nickel-molybdenum alloys are, however, sensitive to oxidizing conditions, they may be employed with aerated media but are unsuitable for sulphuric acid containing oxidizing salts, e.g. acid freely exposed to air, as in the pickling of steel. The addition of chromium to the nickel-molybdenum series produces alloys which resist the action of acid under oxidizing conditions.

In dealing with sulphuric acid we must again consider the austenitic chromium-nickel stainless steels, which are useful for certain concentrations of sulphuric acid. Those containing 2 or 3 per cent of molybdenum, viz. AISI 316 and 317 Types are generally chosen. These compositions with higher normal alloy content and a copper addition have been evolved for dealing with certain concentrations of sulphuric acid and are preferable to nickel-copper alloys for handling sulphuric acid of intermediate concentrations under oxidizing conditions. Under non-oxidizing conditions, however, the nickel-copper alloys are chosen.

CONCLUSION

Corrosion is one of the most serious problems confronting the chemical engineer. It is very unlikely that a single alloy which will offer a satisfactory degree of resistance to all chemical products will ever be produced commercially. Stainless steels are certainly not a panacea for all the corrosion headaches which beset the chemical engineer, but their intelligent use can help a great deal. When faced with conditions for which stainless steels are unsuitable, the chemical engineer can—and usually does—turn to nickel and nickel alloys which, although more expensive, enjoy a high reputation for meeting tough operating conditions. Expert advice is often necessary in selecting the correct alloy due to so many variables affecting corrosion resistance.

Design Problems in Corrosion Engineering

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The importance of design in the prevention of metallic corrosion in the chemical industries has been outlined. The problems of design in corrosion engineering have been discussed with special reference to economics, electrochemical theory, process and structural design, materials of construction and protective measures.

The problem of metallic corrosion and its prevention is one of vital importance to all advanced countries. With the increasing use of metals for various purposes and in different industries, it is imperative that the metal resources of a nation should be conserved and properly utilized by preventing or minimizing the losses due to corrosion wherever it occurs. This is especially so in the chemical industry. The designers of chemical plant are apt to choose the reaction conditions so that the reaction can be carried out in a vessel that can be made economically without taking into account the problem of corrosion. The materials of construction are selected on the basis of initial cost, cost of maintenance and ultimate life. The shape, size and layout of the vessels and ancillary equipment are chosen so that corrosion is reduced to a minimum and maintenance is not a problem. Even though it is often difficult to assess in advance the corrosivity in a particular case, certain fundamental precautions which apply to nearly all service applications can be incorporated in the initial design.

Corrosion is harmful in two ways: (*i*) it reduces the strength of containers and hence their useful life, and (*ii*) the products of corrosion might contaminate the final product. These are the two main results of corrosion which the engineer must attempt to reduce or eliminate. Hence, the fabricator of equipment must keep in mind that corrosion should be eliminated or reduced.

In cases where products of high purity are required, the reaction must be carried out so that no corrosion occurs. A safe material of construction has to be chosen and the choice is based firstly on materials which will be unaffected by the environment, and secondly on physical requirements such as strength and heat transfer. Where contamination is not a serious problem the life of a plant is of major significance. For ensuing maximum benefit, the plant should be of minimum adequate design, which can be determined only by having a comparative idea of the costs for alternative

designs. The major factors involved are initial cost of the equipment, ease and hence the cost of erection and replacement, expected life and hence the rate of depreciation, and the cost of maintenance. These factors are generally helpful in taking decisions on design for reducing corrosion to the minimum. In India, chemical industries have been expanding rapidly during the post-war period, and will grow further as a result of the Five-Year Plans of the government. It is obvious that, while dealing with them one should lay sufficient stress on design of plant and equipment in order to reduce the losses due to corrosion.

ECONOMIC ADVANTAGES

The economic advantages of corrosion prevention methods are well known. It is unnecessary here to go into the figures relating to the losses due to corrosion. A good portion of the losses in each country can, however, be prevented by paying attention to the design engineering. Whitton[1] has recently discussed the costs for two processes having an expected commercial life of four and ten years. He has estimated that, in the first case, the total capital and operating costs using mild steel and stainless steel respectively are: £6,600 & £10,400 and £2,180 & £3,430 respectively. The corresponding figures in the second case are: £16,500 & £ 10,400 and £ 2,180 & £ 1,870 respectively. Mild steel is preferable for the process with a life of four years, whereas it is advantageous to use stainless steel for the other process. An example of this type shows that decisions on design and materials of construction should be based on costs. In large plants the differences between the cost of using a cheap and an expensive material can be considerable, and can also significantly affect the economics of the process. In a competitive world, the design engineer cannot say that it will be safe to use stainless steel. He must test the various alternatives using the corrosion data available and, if necessary, experiment to get more data, so that the decision he makes is based on economic data and is not just a guess.

It is not easy to predict service life from the results of corrosion tests. One important factor in adopting methods for controlling corrosion is that the cost of the measures taken usually has to be met at the outset and the benefits are normally spread over the whole life of the asset. In the field of corrosion, research in economic aspects is just as important as in scientific aspects.

ELECTROCHEMICAL THEORY

Corrosion occurs when a metal or nonmetal reacts with its environment. Corrosion commonly encountered in service is of an electrochemical character in most cases. Reactions occur between two different portions

of the metal surface, and can be represented as follows, for a bivalent metal M, this type of corrosion being classified as the common 'hydrogen evolution' type:

$$2H^+ + 2e \rightarrow H_2 \text{ (cathode)} \quad (1)$$

and $$M \rightarrow M^{++} + 2e \text{ (anode)} \quad (2)$$

If oxygen is present, the reaction

$$O_2 + 2H_2O + 4e \rightarrow 4\,OH^- \quad (3)$$

takes place, and this is 'oxygen depolarization' type of corrosion. When these reactions occur at the same area of the metal surface, the corrosion which occurs is termed 'chemical corrosion'. Electrochemical corrosion is based on the postulate that there is heterogeneity over different parts of the same metal surface due to differences in composition, stress or strain, and heat treatment, and non-uniformity due to imperfect preparation. The designer has little control over the homogeneity of the metals which will be used. It is, therefore, fortunate that under most service conditions inhomogeneities in environment normally are more important sources of potential differences and, therefore, of corrosion than are inhomogeneities in the metals employed. Cathodic and anodic protection are the methods adopted for prevention of this type of corrosion.

PROCESS AND STRUCTURAL DESIGN

In chemical process equipment the problem of minimizing corrosion damage by correlating corrosion data with chemical engineering design is very important. Frequently, the design phase of plant construction is done by engineers who are not experts in the field of corrosion or who have limited knowledge of proper methods of corrosion prevention. Since the corrosion specialists on their side cannot be expected to go deeply into the engineering design of process plants and equipments, there should be some method of communicating their knowledge and experience to the design engineers. Bechtold[2] has suggested corrosion data sheets to bridge this gap, so that potential corrosion problems can be foreseen during the design phase and thus prevented before the equipment is even built. Four corrosion data sheets have been presented by him for basic information, heat transfer equipment, pumps, and pressure vessels. After information of this type has been collected, the problem has to be discussed by the corrosion and design engineers, so that necessary changes in specifications can be made to minimize the possibility of corrosion. Such discussions are also helpful in the choice of proper materials of construction.

The corrosion engineer has to deal, to a large extent, with the investigation of corrosion failures. He is called upon to find a solution to intricate cases of corrosion on the basis of very meagre information. The mechanic

and the operator who are on the site and who know of the changes made and other unusual circumstances, are the ones who provide the information that is needed to solve the problem. Few corrosion failures are identical, and no universal formula can be used to solve all corrosion problems. Furthermore, a condition which is acceptable in one situation may not be so in another. In the diagnosis of corrosion failures, it is essential to understand why the failure occurs, and how a similar failure can be prevented in future. One of the plans suggested[3] for investigating such failures involves the following steps: definition, getting the facts, inspection, analysis, testing, recognition of individual factors, keeping records, literature search, conclusion and report.

The progress of the chemical industry has to a certain extent been controlled by the materials of construction available to the engineer. Hence, considerable thought should be bestowed on construction materials before choosing the process conditions. The factors that have to be borne in mind before handling design can be broadly classified under: (*i*) those inherent in the environment such as galvanic effects, electrolysis, velocity, crevices and deposits, stress corrosion, mass transport; and (*ii*) those which make the environment abnormal such as surface temperature, dewing, aeration-deaeration, oxidizing and reducing agents, water content, corrosion products, local concentrations, blistering, accelerated oxidation-fluxing, attack by gases other than oxygen and by mercury and biological effects[4].

When the designer has chosen the proper material of construction in relation to the specific process, he has to take up the precise form of the design. The structural design of plant, including shape and size of vessel and plant layout, is not of the same order of importance as design of process and choice of materials of construction. The major factors in design of a plant are[1] : (*i*) differential aeration which has to be avoided, (*ii*) contact of dissimilar metals, which leads to galvanic corrosion and hence, has to be avoided, (*iii*) pockets which might retain corrosive chemicals on standby; these have to be avoided by complete draining, (*iv*) inclusion of large manholes for proper cleaning of the vessel, (*v*) provision of facilities for removing condensate from vessel walls as soon after the emptying and opening of a vessel as possible, since thin films in an oxygen atmosphere are often particularly corrosive, (*vi*) residual stresses from fabrication, or stresses formed during plant operation which lead to increased corrosion, and (*vii*) precautions to avoid erosion in corrosive media. The layout of chemical plants also plays an important part in corrosion. A recent trend is to place the plant out in the open, and another to make the plant more compact. In the early stages of design, considerable use is being made of models of plant. Consultation with maintenance engineers with these models may avoid maintenance problems.

The problems in design can be well illustrated with a few examples. The replacement of Monel bolts with stainless alloy bolts in a service in-

volving fuming sulphuric acid resulted in a saving of $ 11,000 per year with practically no increase in the cost of the parts. A plant installed Type 347 stainless steel cascade water coolers to cool inflammable gases at high temperatures and pressures. The stainless steel heat exchangers cost $ 100,000. The Type 347 tubing cracked and leaked after a few months of operation, and the problem was solved by using 4 to 6 per cent chromium steel tubing. Dezincification of brass in relatively mild environments can be overcome by using Admiralty metal or arsenical Admiralty or red brass. Lubricated plug valves often fail in the chemical process industries because of attack on the lubricant by solvents, acids and other chemicals. One solution to this problem is the use of a plug valve where a lubricant is not used[5]. Fontana[6] has recently described corrosion failures in the chemical process industries. They are very costly, unexpected or difficult to explain. A high pressure autoclave was made from Type 304 (18-8S) stainless steel with a 2-in. wall at a cost of $ 20,000. It was actually in operation only for a few days before it developed cracks. A low-alloy carbon steel at a much lower cost was recommended for replacement and was expected to last many years. Numerous cases of stress corrosion of vertical stainless condensers have been solved by proper design and venting to eliminate air or vapour space in the top part of the heat exchanger below the upper tube sheet.

In one case the cast iron impeller of a submerged centrifugal pump became useless in two months of service due to cavitation corrosion. The liquid being pumped—a solution of an organic salt—was only mildly corrosive, but contained sodium sulphate crystals. These crystals tended to settle at the bottom of the tank and starve the pump. Stainless steel solved the problem and was cheaper than redesigning the pump installation. Galvanic action has been reported between the oxide scale and parent metal when mild steel drums were used to pack an agricultural chemical for distribution. The environment was sufficiently corrosive to cause this form of attack. An effective corrosion inhibitor was found, and addition of this to the product before it was charged into the containers prevented corrosion[3].

The corrosion problems encountered in the caustic soda industry with special reference to the D.C.M. Chemical Works, Delhi, have been recently outlined by Pabbi[7]. The corrosion in the brine storage and treating tanks made of mild steel was of the galvanic as well as of concentration cell type, and resulted in deep pitting. The cathodic protection method with zinc anode was not successful in protecting the tanks. A calculation of the costs for an impressed current installation revealed that they were close to the total cost of tanks and vessels. Chemical corrosion plays havoc in caustic evaporators, heat exchangers for evaporators, slurry tanks, salt filters, caustic coolers and interconnecting pipelines. Mechanical cladding is becoming more and more popular and is extensively used in caustic soda evaporators. However, in handling the fabrication of the clad steel vessels,

very great care is needed during cutting, fabrication and welding. The weld has to be free from steel or else a voltaic cell is readily formed in the electrolytes handled. Epoxy resins appear to be satisfactory in brine service, and may prove more economical than cathodic protection.

MATERIALS OF CONSTRUCTION

A wide range of materials is now available for specific operations in the chemical industries. Important data in this connection can be found in a number of recent reviews of a general type[1,8–10], and also with special reference to metals like copper[11], aluminium[12], nickel[13], titanium[14] and tantalum[15]. The common materials of construction are mild steel, chromium, chromium-nickel alloys, nickel, Monel, lead and its alloys, aluminium and its alloys and copper and its alloys. Economic considerations and resources in India make aluminium quite attractive to the plant designer. Amongst the new metals mention may be made of titanium, tantalum, niobium and zirconium. In 1950 the possibility of using titanium as a structural material was hardly considered by any manufacturer. Today it is rapidly establishing itself in the dyeing, bleaching, paper-making and petroleum industries. The cost of lining a mild steel vessel with thin titanium sheet is about twice that of a vessel made wholly of stainless steel. Taking into account the saving in maintenance and saving in time and consequent increase in production, the initial higher cost of titanium can be fully justified in many cases. In spite of the high first cost, tantalum has established itself in the construction of chemical plants, particularly for applications, wherein corrosion resistance has to be combined with a high degree of heat transfer.

The materials of construction for equipment used with hydrogen peroxide have been discussed in great detail by Bloom and coworkers[16]. Glass, polytetrafluoroethylene and tantalum have recently been described as materials of construction for nitric acid concentration. Information concerning corrosion in the oil industry can be found in some recent papers[18–20]. Similar data are available[21] for other chemical process industries such as organic acids and esters, uranium ore processing, for techniques such as filtration, and for equipments such as evaporators, driers, heat exchangers, boilers, pressure vessels and storage tanks.

PROTECTIVE MEASURES

The general methods of preventing or minimizing the corrosion of a metal are by the use of protective coatings—metallic and non-metallic—surface conversion coatings which include anodizing, use of inhibitors in the corrosive medium; and cathodic as well as anodic protection. The choice of the method depends upon the metal, the environment, the degree

of protection offered and the cost. Cathodic[22,23] and anodic[23] protection provide the corrosion engineer with elegant methods for the prevention of metallic corrosion. Cathodic protection of aluminium by the impressed current method[22,24] is of particular interest in India. In addition to magnesium and zinc which are commonly used as galvanic anodes, aluminium and possibly manganese[25] may enter the field. Anodic protection is a new method, and is applicable for the protection of metals like steel and titanium under certain conditions.

CONCLUSION

It is seen from the above discussion that attention to design plays a very important part in the mitigation of corrosion of materials used in the chemical process industries. The corrosion and design engineers can, by mutual consultation, collect the necessary background data on corrosion, choose the proper material of construction, and then design the plant for a specific chemical process. This type of work is of special significance in India, where a beginning is being made to design and fabricate chemical plants with available resources and technical personnel.

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Centrifugal Thin Film Processing Units

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A comparison is made of the design, working, advantages and disadvantages of three different types of thin film processing units, viz. the Luwa, the Sambay and the Kontro types.

Many difficult processing operations are nowadays handled commercially on a continuous and closely controlled basis in the newly developed thin film processing units. When judged by the cost per unit of heat transfer area only, neglecting processing advantages and high coefficients obtained, agitated thin film equipment is more expensive than the conventional units. Some of the salient features of different types of these units are presented in this paper.

Thin film machines spread the material to be processed centrifugally over the heated wall in the form of a thin film maintained under turbulence with rotating, close-fitting blades. The material flows through the unit either by gravity and/or by utilizing a part of the centrifugal force generated.

With a properly designed unit most of the operations can be accomplished continuously and automatically in a few seconds. Consequently, these machines are well suited for heat-sensitive materials. Further, because of the short processing time much higher temperatures are sometimes possible in these units than in other equipment.

TYPES OF PROCESSING UNITS

Three different types of thin film units are available at present. They are: (*i*) the Luwa type, (*ii*) the Sambay type, and (*iii*) the Kontro type.

The first two units (Fig. 1) resemble each other in that both are vertical and straight-sided units. However, they differ from each other in the rotor construction. The Luwa type has uniform one-piece, star-shaped rotor blades, whereas the Sambay type contains individual small blades fixed on the central rotor shaft. The blades are partially free of their movement irrespective of the movement of the rotor shaft. The blades move in such a way that they swing within a certain limit as the rotor rotates. This swing naturally is controlled by the speed with which the central shaft rotates.

Except for this difference in the rotor construction both the Sambay and Luwa types look alike. Both are in the form of long cylinders surrounded

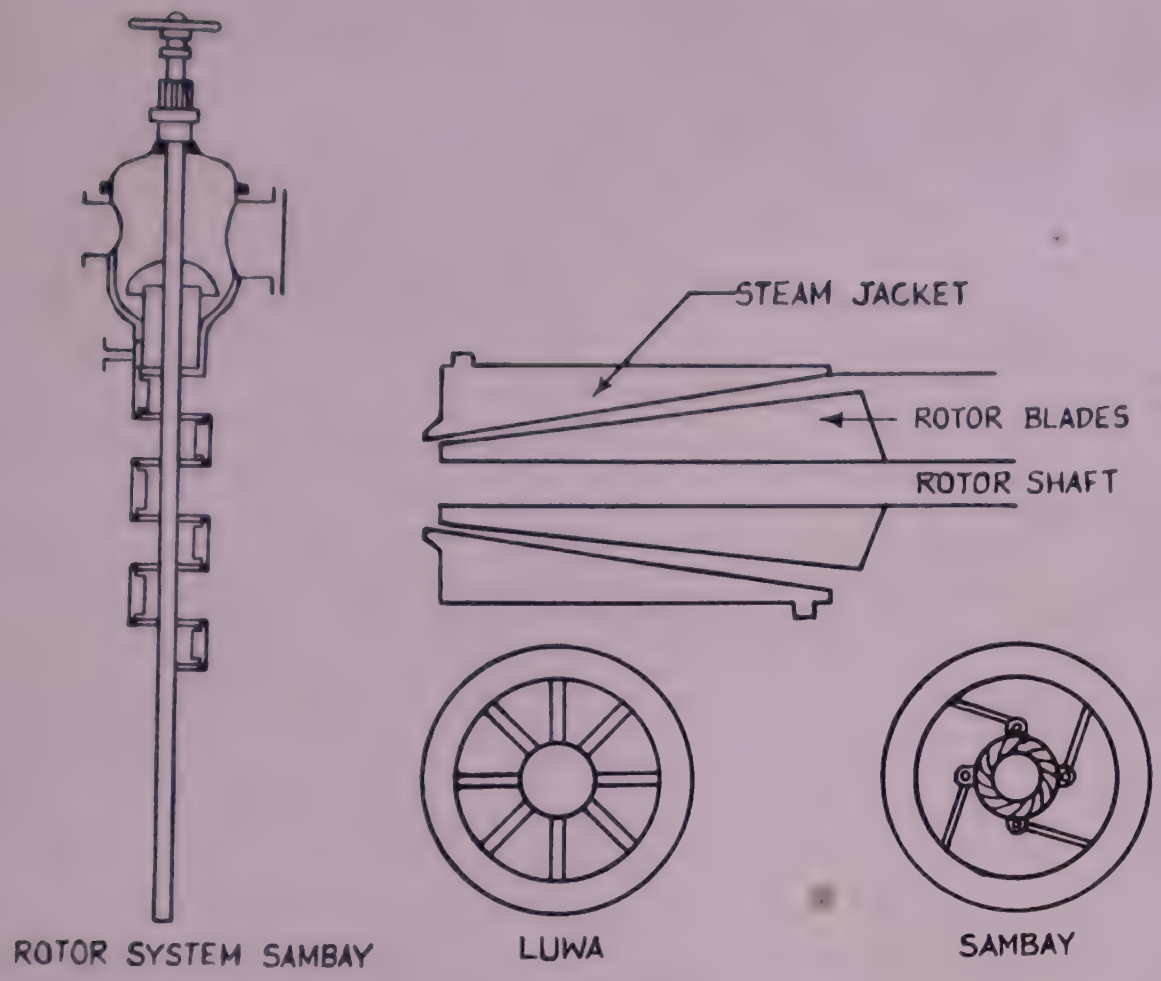

FIG. 1—LUWA AND SAMBAY UNITS

by heating jackets and operate vertically. The thickness of the film formed in these two cases differs. In the case of the Sambay evaporator, the thickness of the film depends on the swinging force exerted by the blades as well as the viscosity of the fluid used. In the case of the Luwa type, however, the swinging force of the blades does not influence the thickness of the film so much as the viscosity of the fluid. Consequently it is easy to appreciate another advantage of the Sambay type over Luwa type. As the Sambay type has individual separable swinging blades different swinging forces can be adjusted upon the different parts of the evaporator body by adjusting the thickness of the different blades from top to bottom. This difference is of very great importance, since nowadays the Sambay evaporators are being used in Germany not only for concentrating a particular material but for drying it to powder also.

The Kontro evaporator is comparatively a recent development and can be said to have gone one step further to the Luwa and Sambay evaporators. The Kontro evaporator has more in common with the Luwa type than with the Sambay type. The Kontro evaporator resembles the Luwa type in having a uniform, one-piece rotor blade system. It differs from both Luwa and Sambay types in that it operates in a horizontal position.

Further, the main evaporator body of a Kontro unit is a 2 in. cone, either forward-tapered or reverse-tapered, surrounded by heating jackets.

The advantage of this cone in a horizontal position can be easily understood. As the unit operates in a horizontal position, the fluid flowing down the heated walls by gravity does not come into the picture. Because of the reverse-tapered cone and the absence of force of gravity, the fluid forces ahead only due to the centrifugal action of the rotor blades. In the case of vertical units the vapours and the concentrated fluid flow countercurrently, whereas in the case of the Kontro unit, the condenser being situated at the far end, the vapour and concentrated product run co-current with respect to each other. Another difference is that, due to the conical construction, a Kontro unit will never be emptied (unless it is drained off) even if the unit is run for a while after the feed is cut off. The Luwa and the Sambay types will be empty in a short while after the feed is cut off completely.

Such types of evaporators are very useful especially for heat-sensitive products because of the short time of residence of the material in the evaporator. Because of the fact that the material passes only once in the thin film units evaporation or the distillation processes are basically different from those of the circulation type evaporators. The separation of a two-component mixture along the entire length of the evaporator is shown in Fig 2. When most of the low-boiling component reaches its boiling point the mixture reaches a temperature t_1. As the mass fraction of the higher boiling component goes on increasing, the film temperature increases, and shoots up towards the end of the evaporator. Thus, the temperature in the evaporator corresponds to the temperature of the mixture, which is quite low at the near end of the apparatus. The product reaches its desired temperature only in the last section of the apparatus. As against this, in a circulation evaporator, the entire apparatus has to be maintained at a particular temperature to arrive at a particular concentration.

A comparison between a Vat boiler, a forced circulation evaporator and a thin film unit is shown below:

Boiler	Circulation evaporator	Thin film unit
Concentration increases with time	Takes some time to reach end concentration	Concentration increases with the length of film
Actual time of residence, 5 to 50 hr	Av. time of residence, 15 to 60 min.	Actual time of residence, 3 to 20 sec.
Time saving	$\frac{1}{50}$ to $\frac{1}{20}$	$\frac{1}{300}$ to $\frac{1}{180}$

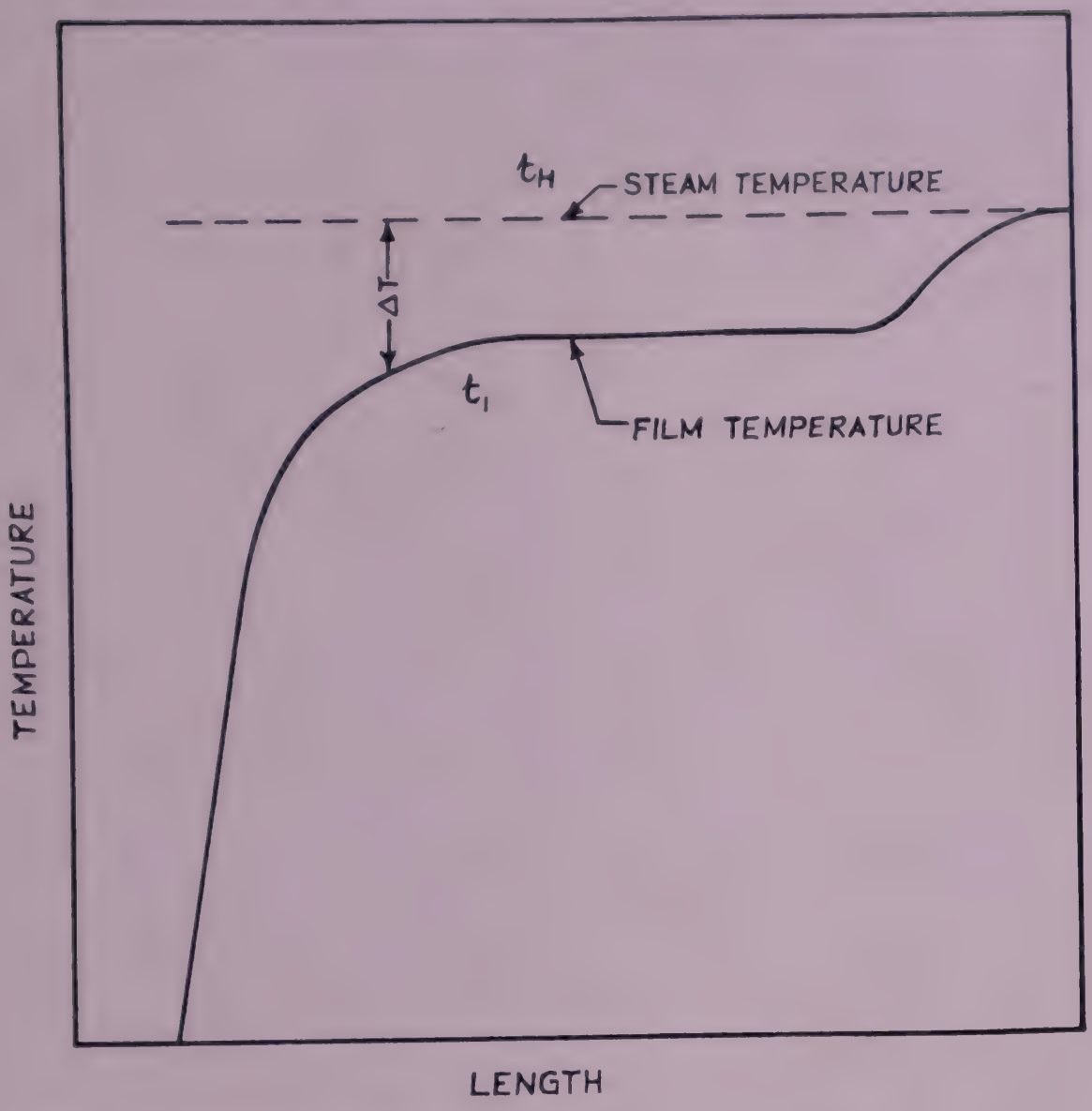

FIG. 2—SEPARATION OF A TWO-COMPONENT MIXTURE ALONG THE LENGTH OF EVAPORATOR

It has been observed in case of the Sambay evaporator that the overall heat transfer coefficients drop down along the length of the evaporator. This is due to the fact that with increase in concentration, the viscosity increases and offers more resistance to heat transfer. For the same concentration, the mean overall heat transfer coefficients are much higher than those obtained with the other evaporation units.

The measurement of film thickness is a difficult problem. In the case of a trial run of an evaporator of 160 mm. diam. the measurement was done in such a way that the unit was run cold without any evaporation taking place. A known amount of fluid was fed in and after a short while the quantities of the outcoming fluids were measured immediately. From these quantities the film thicknesses were calculated. It was observed that the thicknesses of the films were in direct relation to the throughput and

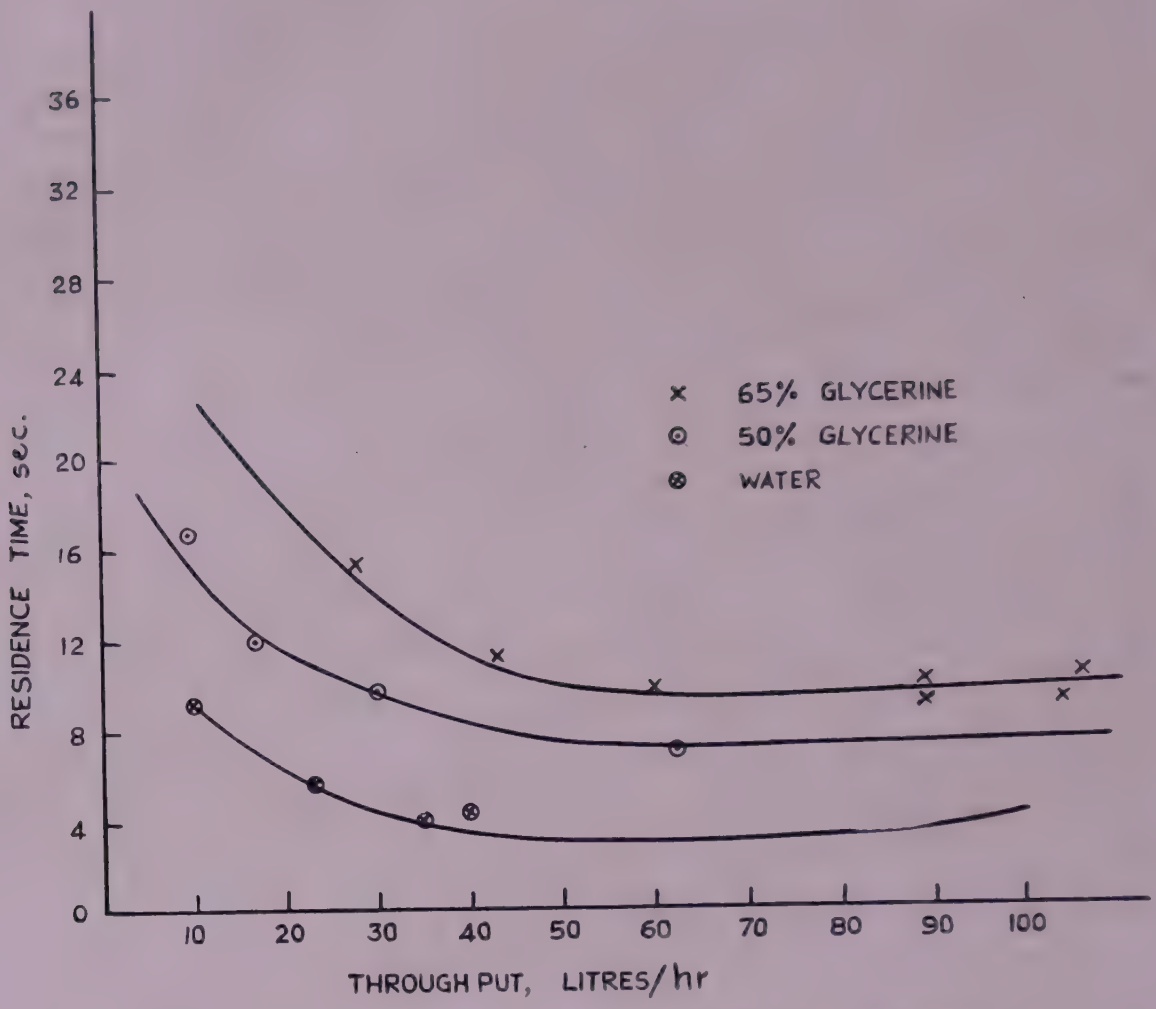

FIG. 3—RELATIONSHIP BETWEEN FILM THICKNESS AND THROUGHPUT

also the viscosity of the material (Fig. 3). In most of the cases the thicknesses lie between a few tenths of a millimetre. In the case of Sambay and Luwa units no definite relationship has yet been established between the overall heat transfer coefficients and the speed of the shaft. In the case of the Kontro units, it is claimed especially by the Kontro Company, that the overall heat coefficients bear a direct relationship with the speed of the shaft. It has, however, been the author's experience that for a particular product a certain minimum speed of the shaft is necessary to get the best results. This is also the case with the vertical units.

The relationship between the throughput and residence time for (*i*) 65 per cent glycerine, (*ii*) 50 per cent glycerine, and (*iii*) water, is given in Fig. 4. The variation of the overall heat transfer coefficient with $\triangle T$, the temperature difference for water with 10 per cent glycerine is shown in Fig. 5.

All these units can be run under very high vacuum. The Kontro pilot plant can be run under elevated pressures. In the Sambay unit the stuffing boxes used are foolproof against high vacuum. The Kontro unit which the author saw in working condition was fitted with 'John Crane'

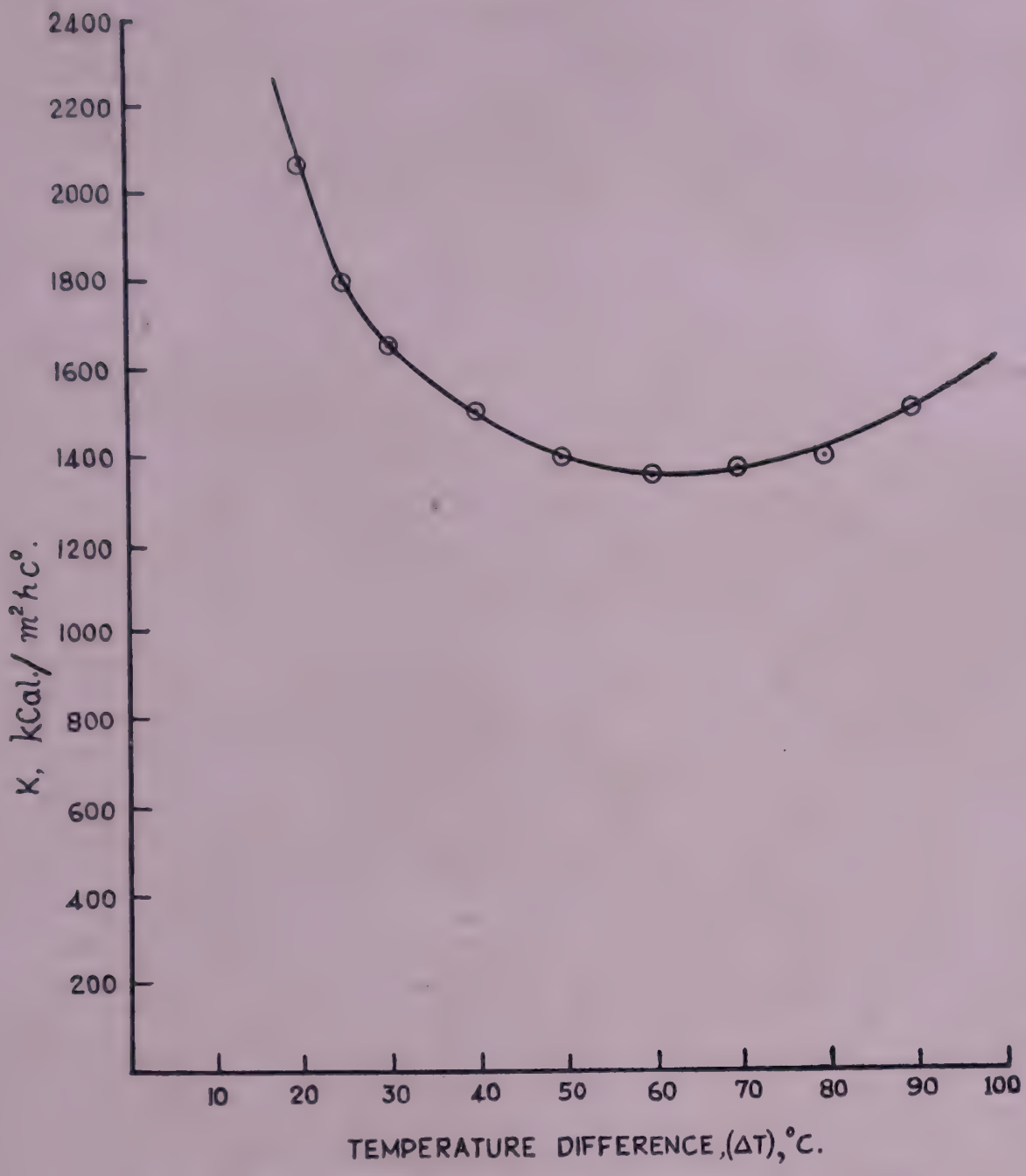

FIG. 4—RELATIONSHIP BETWEEN RESIDENCE TIME AND THROUGHPUT

packings, and seals. The unit had to be kept cooled using pressurized water on the two ends. In the recently developed models of the Kontro unit, instead of the delicate graphite seals a stuffing box on one side and a self-lubricating internal gearing on the other are used.

Most of the general characteristics mentioned above are common in all the three types of units. The Kontro unit differs from the other type of units in that it is a co-current type of evaporator. Moreover, because of this fact, the vapour formed when the product evaporates is superheated. In the Luwa or the Sambay units, a portion of the vapour formed is condensed by the incoming cold feed thereby reducing the heat economy.

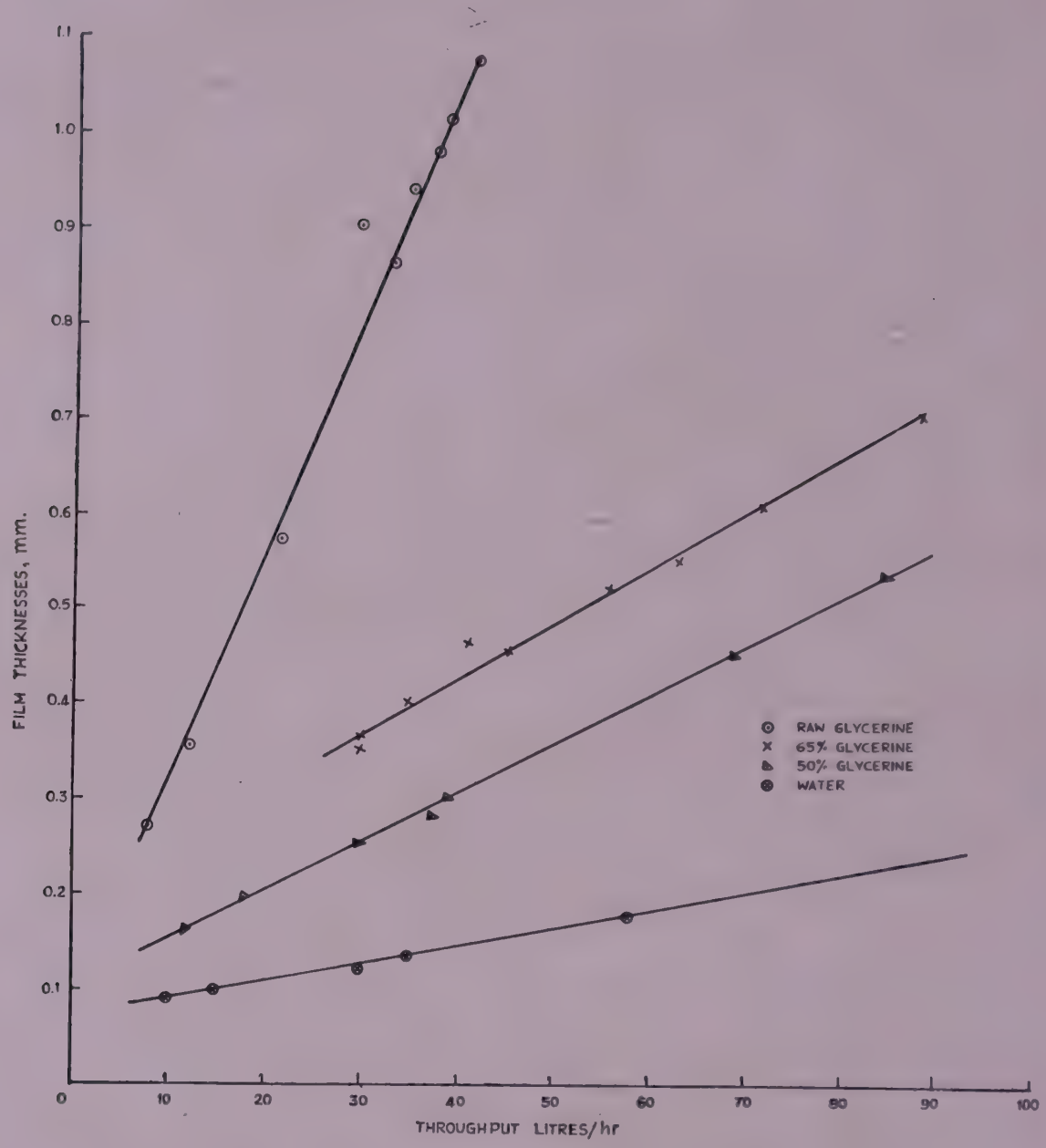

FIG. 5—RELATIONSHIP BETWEEN OVERALL HEAT COEFFICIENT AND $\triangle T$

Thus, in the vertical units an intermediary cold zone exists just around feed inlet. One more advantage of the Kontro unit is that it is fitted with an adjustable rotor which can be shifted from 2 to $3\frac{1}{2}$ in. away. As a result, the thickness of the film can be controlled.

ACKNOWLEDGEMENT

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An Experimental Thin Layer Evaporator

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An experimental thin layer evaporator with 1 sq. ft heating surface has been designed and fabricated. A very effective design of an entrainment separator has been evolved. The unit has been tested by concentrating sugar syrup using different speeds of rotation of the agitator, and heat transfer coefficients have been measured.

Two new types of evaporators (plate and agitated film) have been developed for use in the food industry. The plate type evaporator incorporates the principle of the climbing and falling film evaporators and the agitated film evaporator is based on the falling film type with a mechanical aid for further reduction of film thickness. Each has its own advantages in the particular field of its application.

Ease of construction, provision for variation of heating surface to a certain extent and ease of cleaning the heating surface are some of the features which make the plate type evaporator very promising.

The agitated film evaporators are very well suited when the hold-up time in the evaporator is required to be very short, of the order of a couple of minutes. It has successfully been used for the concentration of fruit juices and purees, tomato juice, coffee and many heat-sensitive pharmaceutical products. Apart from its use as an evaporator, it has been used in many operations involving mass and/or heat transfer—such as deaeration, pasteurization, steam refining of vegetable oils, etc.

Details of standard thin layer evaporators as described by Coston[1] are given in Table 1.

Some of the disadvantages of this type of evaporator are the very large units necessary for higher rates of evaporation as apparent from the table, and the high cost of production due to precision machining and balancing of the rotor and the evaporator body.

Based on these considerations, the Central Food Technological Research Institute, Mysore, set about designing an experimental thin layer evaporator, in order to gain the necessary skill and know-how of construction of such evaporators and to collect performance data and to show that evaporators as good as any imported ones could be constructed locally.

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TABLE 1—STANDARD THIN LAYER EVAPORATORS

Unit	Evaporation capacity *lb./hr*	Length *in.*	Diam. *in.*	Area *sq. ft*	Rotor *h. p.*	Steam consumption *lb./hr*
Lab. size	40	42	9·5	1	0·50	50
1	150	72	16·0	4	1·50	180
2	300	107	26·0	9	2·00	330
3	600	143	26·0	18	3·00	720
4	1,200	162	42·0	33	5·00	1,400
5	2,500	222	42·0	66	7·50	3,000
6	5,000	300	64·0	142	10·00	6,000

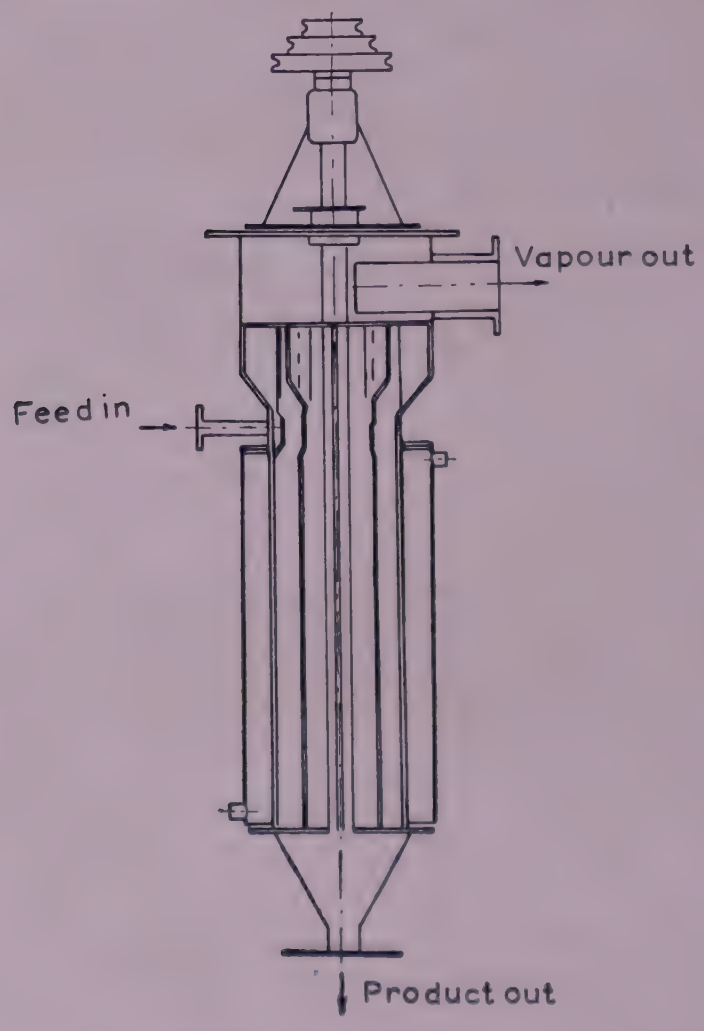

Fig. 1—Experimental thin layer evaporator

DESIGN OF THIN LAYER EVAPORATOR

The evaporator (Fig. 1) consists of a vertical, jacketed cylinder with a central rotor carrying vertical fins which rotate with a clearance of 1/32 in. between the fins and the wall. Steam is circulated in the jacket. The feed enters at the top of the heating zone and flows down the heated sides of the cylinder and the cylindrical rotor having six fixed radial blades wipes the liquid from the surface such that only a thin film of liquid is maintained on the cylinder side. The heating surface is one square foot in area.

All the parts coming into contact with the material are made of Type 316 stainless steel. The jacket is also made of highly polished stainless steel to minimize radiation losses and prevent rusting. The jacket is designed to withstand a steam pressure of 50 lb. per sq. in. with 27 in. vacuum inside the chamber. A baffle is placed at the steam inlet to prevent direct impinging of steam thereby reducing erosion and preventing local heating. The inside wall is made of 3 mm. stainless steel sheet, highly polished both on the inside and outside.

As the evaporator has to be thoroughly cleaned after every operation, the rotor assembly is so designed that it can be taken out without disturbing the other connections. Corners where material accumulates have been rounded off and polished. The bottom is easily removable for flushing with water. Care has been taken to eliminate contamination of the liquid handled, by grease and other lubricants used in the stuffing box. The bottom bearing which also acts as a support to the rotor is an oilless bearing. The rotor can be run at speeds between 500 and 2000 r.p.m., to enable study of the

TABLE 2—PERFORMANCE DATA OF THIN LAYER EVAPORATOR

(*Steam pressure*, 15 *lb./sq. in.; vacuum*, 25 *in.*)

R.P.M.	Concentration, *Brix* (sugar)		Feed rate *lb./hr*	Heat transferred *B.t.u./hr/sq.ft/°F.*
	Initial	Final		
550	11	40	54·5	313
550	10	85·7	33·2	250
550	10·5	28	81·6	438
880	10	44	57·6	394
880	10	23	83·6	392
1,400	10	43	57·0	391
1,400	10	31·5	82·6	482
2,000	10	58	55·0	400
2,000	10	63	53·0	380

variation in heat transfer at different speeds. The rotor extends into vapour chamber above the heating chamber. A set of fixed baffles are located in this chamber which intercept the droplets and foam and thereby reduce entrainment. Entrainment is completely eliminated by extending the vapour outlet pipe up to the centre of the chamber. The feed enters through a 10 mm. diam. tube in between the vapour chamber and evaporator tube. The 25 mm. outlet for concentrate is located in the conical lower section, which also houses the bottom bearing of the rotor. A ten sq. ft condenser is attached to the evaporator to condense the vapour. The evaporator itself requires about 60 lb. of stainless steel and 400 man-hours of labour (costing *c.* Rs 1,500). With accessories, the complete unit will cost about Rs 5,000.

Performance data of this thin layer evaporator are given in Table 2.

Further improvements in the design are proposed to be investigated; they are: (*i*) the use of hinged-wiper rotor which wipes the surface in place of the fixed rotor, (*ii*) change of the feed entry and concentrate outlet positions in order to reduce the resistance to the flow of liquid, and (*iii*) change of the steam inlet into the jacket into a tangential entry to let only dry steam approach the condensing surface and thereby increase the heat transfer.

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Process Design of a Fluidized Bed Reactor for Producing Phthalic Anhydride from Naphthalene

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The principles of reactor design for the manufacture of phthalic anhydride (capacity, 3 tons/day) by vapour phase oxidation of naphthalene using vanadium pentoxide as catalyst in a fluidized reactor have been discussed. The influence of process variables on the design has also been discussed.

The oxidation of naphthalene to phthalic anhydride is a highly exothermic reaction to which the fluo-solids technique has been successfully applied in industry. The design of the reactor for this purpose had, so far, to be based on empirical methods. An attempt has been made to outline in this paper a procedure for the design of an isothermal fluidized bed reactor using the limited published data on kinetics of the reaction and on continuous fluidized reactors. Various process variables encountered in design of the reactor have also been discussed.

MECHANISM OF REACTION

Several workers have studied the kinetics of oxidation of naphthalene to phthalic anhydride using solid catalysts. The mechanism proposed by Sherman and Ioffe[7] is shown in Fig. 1. These authors concluded that the reaction rate is controlled by diffusion of reactants to the catalyst. Oftentimes, fast reactions can be taken as diffusion controlling and so it is possible to arrive at the height of transfer unit (HTU) and number of transfer units (NTU), and thus calculate the reactor volume.

Pinchbeck *et al.*[3] arrived at a conclusion contrary to the above, viz. that the reaction rate is controlled by surface kinetics. They further stated that the oxidation of naphthalene is a fractional order reaction.

For a complex set of reactions, such as the one shown in Fig. 1, it is indeed difficult to determine the rate constants of the individual chemical steps. Empiricism was therefore sought by Franklin *et al.*[2,4] who correlated five process variables, viz. the ratio of air to hydrocarbon, contact time, temperature, apparent density of the catalyst and the ratio of the moles

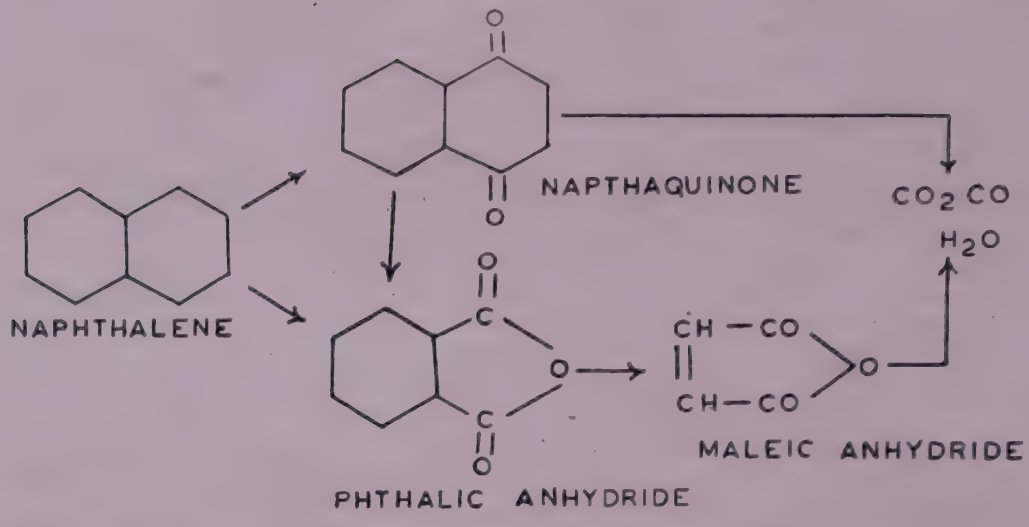

FIG. 1—REACTION MECHANISM PROPOSED BY SHERMAN AND IOFFE

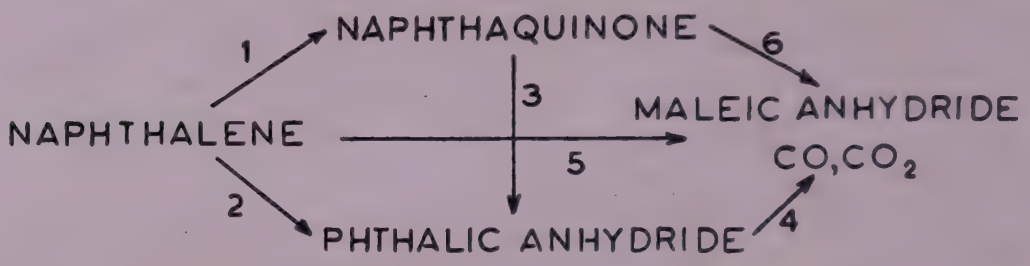

FIG. 2—REACTION MECHANISM PROPOSED BY DE MARIA *et al.*

of the catalyst to the moles of the moderator added to avoid over-oxidation. The yield of phthalic anhydride (YPA) is thus given by Equation (1):

$$\begin{aligned} \text{YPA} = {} & -292{\cdot}9+137{\cdot}36x_1+221{\cdot}37x_2+247{\cdot}75x_3 \\ & +20{\cdot}44x_4+46{\cdot}14x_5-17{\cdot}91x_1^2-48{\cdot}35x_2^2 \\ & -38{\cdot}65x_3^2-9{\cdot}17x_4^2-14{\cdot}09x_5^2-13{\cdot}23x_1x_2 \\ & -47{\cdot}90x_1x_3-6{\cdot}04x_1x_4-10{\cdot}9x_1x_5-81{\cdot}24x_2x_3 \\ & -11{\cdot}63x_2x_4-18{\cdot}74x_2x_5-12{\cdot}66x_3x_4 \\ & -15{\cdot}1x_3x_5+27{\cdot}95x_4x_5 \end{aligned}$$

where

x_1 = $\log_{10}$ (ratio of air to naphthalene, litres/g.)

x_2 = $\log_{10}$ (contact time, sec. $\times 10$)

$$x_3 = [\text{temperature (°C.)} - 330] \times \frac{1}{100}$$

$$x_4 = \left(\frac{10}{\text{apparent density}}\right) - 4$$

$$x_5 = 5 \times \frac{\text{moles of } V_2O_5}{\text{moles of } K_2SO_4}$$

The work of De Maria *et al.*[1], however, indicates that the oxidation of naphthalene, though fast, is controlled by the relative rates of the reactions involved. The mechanism suggested by them is shown in Fig. 2. The

reactions leading to the formation of maleic anhydride from naphthalene and from naphthaquinone have negligible rates under normal operating conditions. Consideration of the remaining four reactions gives rise to the following equations:

$$-\frac{d}{d\theta}(\rho C_N) = (k_1+k_2)\,\rho^2 C_N Co_2 \tag{2}$$

$$-\frac{d}{d\theta}(\rho C_Q) = -k_1\rho^2 C_N Co_2 + k_3\rho^2 C_Q Co_2 \tag{3}$$

$$-\frac{d}{d\theta}(\rho C_P) = -k_2\rho^2 C_N Co_2 - k_3\rho^2 C_Q Co_2 + k_4\rho^2 C_P Co_2 \tag{4}$$

Due to the large excess of air used in practice, the concentrations of oxygen and carbon dioxide and the molal gas density, ρ, may be assumed to be non-variant. Then the above equations are respectively simplified to:

$$-\frac{dC_N}{d\theta} = (k'_1+k'_2)C_N \tag{5}$$

$$-\frac{dC_Q}{d\theta} = -k'_1 C_N + k'_3 C_Q \tag{6}$$

$$-\frac{dC_P}{d\theta} = -k'_2 C_N - k'_3 C_Q + k'_4 C_P \tag{7}$$

where k'_1, k'_2, k'_3 and k'_4 are the respective pseudo first order rate constants. The values of these constants in the temperature range, 320–370°C., are given by the above authors.

PROCESS VARIABLES IN A FLUIDIZED BED REACTOR

Low radial temperature gradients, better temperature control, low ratio of air to hydrocarbon and simpler heat removal favour the use of fluidized beds rather than the fixed beds.

The variables in a continuous fluidized bed reactor may be classified into two categories: (*i*) those affecting the physico-chemical properties of the system, and (*ii*) those affecting the residence times of the gas and the catalyst particles.

Examples of the first category of variables are catalyst, pressure, ratio of air to hydrocarbon and temperature.

Examples of the second type are the ratio of length to diameter (L/D) of the reactor, gas distribution system, solids introduction system and ratio of operating gas velocity to the terminal velocity of the particles in the gas. De Maria *et al.* constructed an eddy diffusivity model and studied back-mixing as a function of Peclet number. A great deal of work is yet to be

done to explore fully the effects of all variables on the gas flow pattern and the frequency distribution of the solids residence time. Under present conditions it is possible to design theoretically only narrow reactors wherein plug flow conditions may be approximated.

CONSIDERATIONS FOR DESIGN OF REACTOR

(i) **Catalyst.** The catalyst used is vanadium pentoxide supported on silica gel, with potassium sulphate added to avoid over-oxidation. As too fine a size of catalyst gives lesser yields and more recovery troubles, catalyst of the size range 40–80 mesh is used in practice.

(ii) **Ratio of Air to Hydrocarbon.** The data of Mars and Krevelen[5], Calderbank[6], Ioffe and Sherman[7] and Shelstad, Downie and Grandon[8] show that below an oxygen partial pressure of 300–400 mm. of mercury, the rate of naphthalene conversion is almost proportional to the concentration of oxygen; and that the rate is roughly of the first order with respect to naphthalene when its partial pressure is less than 4 mm. of mercury and is independent of naphthalene concentration when its partial pressure is above 8 mm. of mercury.

Considerable excess of air is used in order to maintain proper yield and purity. In actual practice, 15 lb. of air are used for 1 lb. of naphthalene. This corresponds to an oxygen partial pressure of 157 mm. of mercury and a naphthalene partial pressure of 11·3 mm. of mercury in feed. Due to the large excess of oxygen, zero order kinetics with respect to this reactant are often approximated.

(iii) **Temperature.** Under certain conditions, the temperature versus yield of phthalic anhydride curve shows a maximum value, below which the oxidation is incomplete and above which over-oxidation prevails. The reaction temperature can be lowered with higher initial concentrations of the hydrocarbon in the feed. The operating temperature in industrial reactors is normally within the range 360–385°C.

(iv) **Residence Time* of Gas.** In order to predict the exact composition of the product, it is essential to have at hand a detailed picture of the gas flow pattern. However, in the absence of such description pseudo-integral reactor conditions may be approximated without introducing large errors, if the L/D of the reactor is very large. This method is employed in the calculations given below, to show the effect of residence time on the product distribution:

Equations (5), (6) and (7) are integrated to give the following expressions:

$$C_N = a_1 e^{\beta_1 \theta} \tag{8}$$

$$C_Q = a_2 e^{\beta_3 \theta} + a_3 e^{\beta_1 \theta} \tag{9}$$

$$C_P = a_4 e^{\beta_3 \theta} + a_5 e^{\beta_1 \theta} + a_6 e^{\beta_3 \theta} \tag{10}$$

*The residence time of solids is discussed under 'Hold up'.

where

$$a_1 = C_N^\circ$$

$$a_2 = C_Q^\circ - \frac{k_1' a_1}{k_3' + \beta_1}$$

$$a_3 = \frac{k_1' a_1}{k_3' + \beta_1}$$

$$a_4 = C_P^\circ - \frac{k_2' a_1 + k_3' a_3}{k_4' + \beta_1} - \frac{k_3' a_2}{k_4' + \beta_2}$$

$$a_5 = \frac{k_2' a_1 + k_3' a_3}{k_4' + \beta_1}$$

$$a_6 = \frac{k_3' a_3}{k_4' + \beta_2}$$

$$\beta_1 = -(k'_1 + k_2')$$

$$\beta_2 = -k'_3$$

$$\beta_3 = -k'_4$$

The reactor feed is taken as naphthalene and air in the ratio of 1 : 15 by weight. A temperature of 360°C. is chosen, and the values of the pseudo-first order rate constants (sec.$^{-1}$) read from graph[1]:

$k_1' = 2{\cdot}03$; $k_2' = 2{\cdot}03$; $k_3' = 5{\cdot}45$; and $k_4' = 0{\cdot}025$

Substituting the numerical values, Equations (8), (9) and (10) are reduced to:

$$C_N = 0{\cdot}0149\ e^{-4{\cdot}06\theta}$$

$$C_Q = 0{\cdot}02175\ [e^{-4{\cdot}06\theta} - e^{-5{\cdot}45\theta}]$$

$$C_P = 0{\cdot}01418\ e^{-0{\cdot}025\theta} + 0{\cdot}0218\ e^{-5{\cdot}45\theta} - e0{\cdot}0361\ e^{-4{\cdot}06\theta}$$

Using these equations, percentage conversion of naphthalene at different residence times have been calculated and the values have been plotted in Figs. 3 and 4. It is seen that beyond a residence time of 2 sec. the yield curve for phthalic anhydride more or less remains flat. Hence, a residence time of 2 sec. may be chosen as optimum.

(v) **Operating Gas Velocity (u_g).** With the help of the results obtained in (*i*) (*ii*), and (*iii*) and an experimental determination of the apparent density of the catalyst, the terminal velocity, u_t, may be calculated using Equation (14):

$$u_g = a u_t \tag{14}$$

where a is a constant chosen in the range, 0·8–0·9.

(vi) **Diameter of Reactor (D).** Since the residence time is fixed at 2 sec., the corresponding value of C_P may be obtained from Fig. 3. Hence, from the capacity, the total throughput of gas can be calculated. If Q is the total volumetric flow rate of the gas, then:

$$Q = \frac{\pi D^2}{4}\ u_g \tag{15}$$

from which the value of D is obtained.

(vii) **Height of Reactor.** If θ is the residence time for the gas,

$$\frac{\pi D^2}{4} u_g \theta = \frac{\pi D^2}{4} L \left(1 - \frac{\epsilon_s}{100}\right)$$

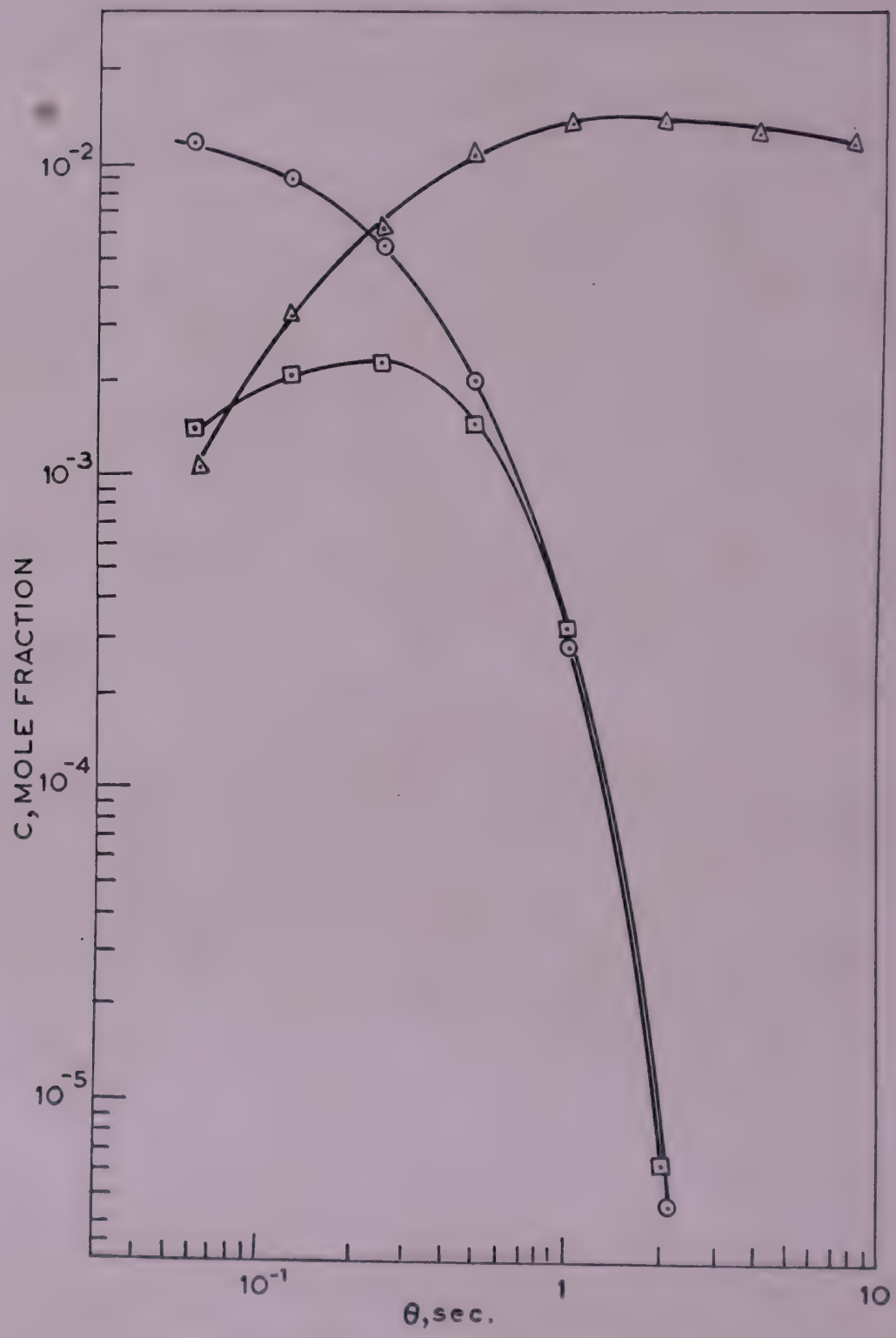

FIG. 3—EFFECT OF RESIDENCE TIME ON PRODUCT DISTRIBUTION

○ Naphthalene ▫ Naphthaquinone △ Phthalic Anhydride

$$\therefore L = \frac{u_g \theta}{\left(1 - \frac{\epsilon_s}{100}\right)} \tag{16}$$

The value of ϵ_s has to be fixed at the maximum possible for the system under the operating conditions. For dense-phase beds, its value varies from 1 to 25 per cent.

(viii) **Solids Flow Rate.** To provide high bed densities and thereby reduce the size of the reactor, continuous dense-bed fluidization conditions are employed. Sarma, Sen Gupta and Rao[9] correlated bed densities in the dense phase, through dimensionless groups in the form of the following equation:

$$\epsilon_s = 19 \left\{\frac{r\, D_p\, g_c\, \rho_s}{u_g^2 \quad \rho_g}\right\}^{0.244} \left\{\frac{L}{D}\right\}^{-0.38} \tag{17}$$

From this equation, the value of the solids loading ratio (r) is computed, and since

$$r = \frac{\text{solids mass flow rate}}{\text{gas mass flow rate}}$$

the catalyst circulation can be calculated.

(ix) **Catalyst Hold-up and Residence Time.** The catalyst hold-up (W) is given by Equation (18):

$$W = \frac{\pi D^2}{4} L \left(\frac{\epsilon_s}{100}\right) \rho_s \tag{18}$$

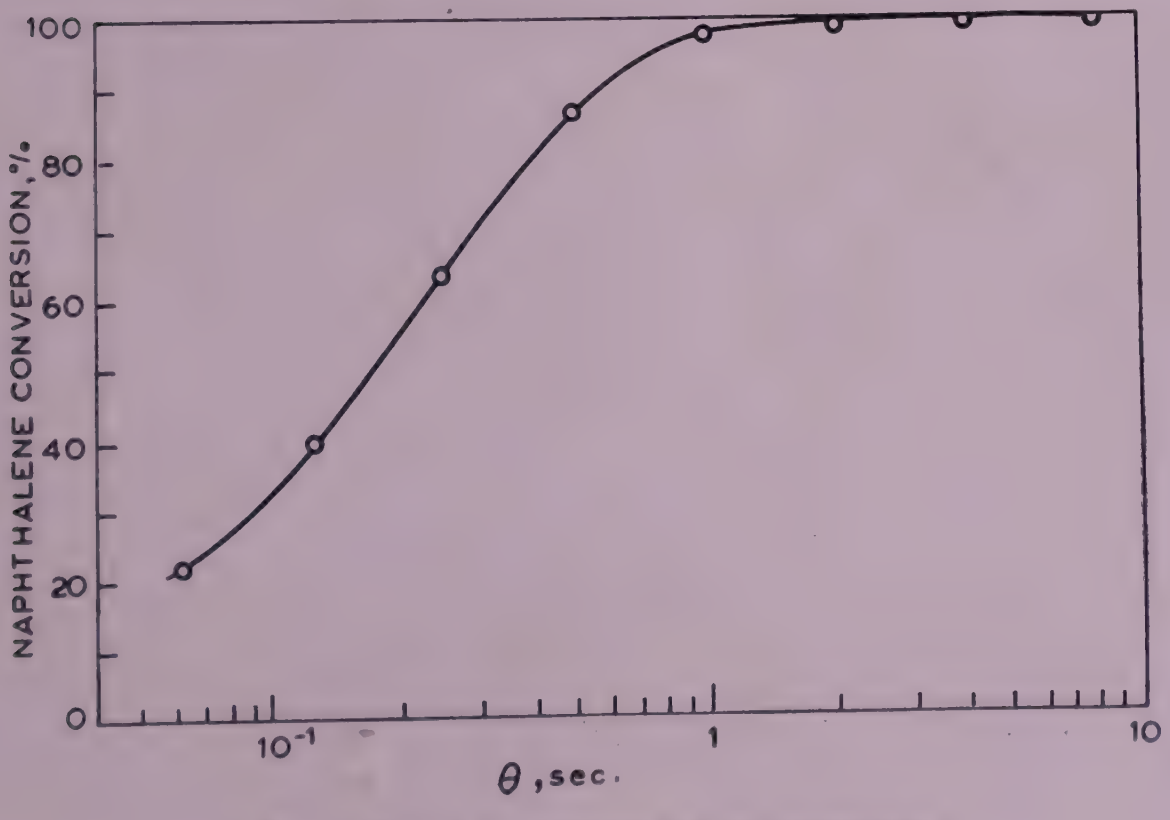

FIG. 4—EFFECT OF RESIDENCE TIME ON CONVERSION

If θ_s is the residence time for solids,

$$\frac{R}{\rho_s}\,\theta_s = \frac{\pi D^2}{4}\,L\,\frac{\epsilon_s}{100} \tag{19}$$

The value of θ_s is obtained from Equation (19) and then it is checked that the value of L/θ_s is reasonable, i.e. it should be less than u_g.

Values for a typical Plant

Plant Capacity. three tons of 99·9 per cent pure phthalic anhydride/day

(*i*) *Parameters fixed:*
Process, isothermal
Yield of phthalic anhydride, 95 per cent
Av. size of catalyst particles, 0·00077 ft
Air: naphthalene ratio (by wt), 15
Temperature, 360°C.
Residence time for gas, 2 sec.
u_g/u_t, 0·8
Percentage of solids in reactor, 10
Apparent density of catalyst, 116 lb./cu. ft

(*ii*) *Parameters calculated:*
Height of reactor, 7·23 ft
Diameter of reactor, 3·45 ft
Operating gas velocity, 4·08 ft/sec.
Rate of circulation of catalyst, 43·1 lb./hr
Residence time of catalyst, 18·2 hr.
Catalyst hold-up, 788 lb.
Naphthalene conversion, 99·97%

Nomenclature

a = Numerical constant
C_A = Mole fraction of the component A (subscripts N—naphthalene; Q—naphthaquinone: P—phthalic anhydride; O_2—oxygen)
C_A^o = Mole fraction of component A in feed
D = Diameter of reactor, ft
D_p = Diameter of catalyst particle, ft
g_c = Gravitational constant
k_1 = Rate constant for the reaction, naphthalene→naphthaquinone, cu.ft/(lb. moles) (sec.)
k_1' = Pseudo first order rate constant for the reaction, naphthalene→naphthaquinone, $sec.^{-1}$
L = Height of fluid bed, ft

Q = Quantity flow rate of gas, cu.ft/sec.
R = Quantity flow rate of catalyst, lb./sec.
r = Ratio of solids flow to gas flow (by weight)
u_g = Operating gas velocity, ft/sec.
u_t = Terminal velocity of the catalyst particles in the fluidizing medium, ft/sec.
W = Catalyst hold-up in reactor, lb.
ϵ_s = Percentage of solids in the fluid bed
θ = Residence time for gas, sec.
θ_s = Residence time for catalyst, sec.
ρ = Molal density of the gas, lb. moles/cu. ft
ρ_g = Density of the gas, lb./cu.ft
ρ_s = Apparent density of catalyst pellets, lb./cu.ft

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Some Important Aspects of Fluid Beds

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The technique of fluidization and its various phases, such as incipient, expanding and moving bed fluidization, have been explained. Applications of the technique in industrially important catalytic reactions have been elaborated. Further, major problems like the bubble phenomenon, heat transfer and scaling up of models which have not yet been satisfactorily solved for the greater success of the technique have been discussed.

The term 'fluidization' owes its origin to a certain mode of contacting of solid discrete particles with fluids. As the velocity past a column of solid particles resting on a false bottom is gradually increased, a stage is reached when the particles are just kept in suspension. At this point, the pressure drop in the bed equals the buoyancy of the bed particles. Further increase in the fluid velocity would expand the bed uniformly in the absence of channelling action of fluid through particle interstices. The expansion would continue with continual increase in the fluid velocity until another limiting velocity is reached when the particles would no longer tend to expand but would be borne away in a continuous manner by the current of gas or liquid. These three phases of fluidization are termed as incipient, expanding and moving bed fluidization respectively, while boiling, dense and rare phase beds are terms evolved for characterizing one or more of the above phases.

The gas-solid fluid bed is applicable to all vapour phase catalytic reactions where free-flowing, non-sticky, granular solid particles are in contact with gases. The main advantages of the fluid bed are its (*i*) ability to attain isothermal conditions, (*ii*) adaptability to continuous operations, and (*iii*) heat transfer efficiencies[1].

The fluidization technique is the outcome of developmental efforts of the petroleum industry. The work on fluid beds was initiated by Kellog Co. and Standard Oil of Indiana as part of their drive towards finding a superior catalytic cracking process. The first fluid bed catalytic cracking plant was put into operation in 1942. The packed bed method which was formerly considered as a major improvement over the thermal cracking process has since been replaced by the fluid bed technique.

The applicability of the fluid bed in the production of ethylene oxide[2] from ethylene, and alkyl chlorides[3] from reaction of chlorine with olefins are some of the later discoveries. There are quite a number of other oxidation

processes which can employ the fluid bed technique to obtain the end products most economically, and the productions of phthalic[4] and maleic[5] anhydrides are two such examples. The advantages of the fluid bed have been commercially exploited by adapting it in catalytic dehydrochlorination, chlorination, dehydration and dehydrogenation. Examples are production of vinyl chloride[6] from ethylene dichloride, aluminium chloride[7] from bauxite and chlorine, ethylene[8] and ether[9] from alcohol, and cymenes from carenes respectively. It has also been employed in accomplishing limestone calcination[10,11], roasting of iron[12] and gold[13] ores, manufacture of carbon black, production of water gas, coal gasification[14] and construction of nuclear reactor[15]. However, the application of the fluid bed principle to drying, dyeing, curing, etc. of textiles and paper is of recent origin, and it is an outcome of research and developmental activities of the Shri Ram Institute for Industrial Research[16], India, and British Rayon Research Association[17], U.K.

Investigations in these two research organizations have shown that drying of sheet materials can be accomplished by employing fluid beds mainly in two ways. Piece-goods like cardboards are dried by dipping the material in the bed while long sheets like textiles and paper are dried by passing the material in a continuous fashion. The latter method employs equipment of two kinds, viz. (*i*) an apparatus wherein the material is first led down the bed of hot fluidized particles and then upwards through a guide roller situated at the bottom, and (*ii*) an apparatus wherein the material is led from the bottom to the top. But the presence of a thin sheet of material in either types of equipment divides the bed into narrow columns, thus posing serious mechanical problems in the continuous operation of the plant. Further, improper fluidization caused by bubble phenomenon and non-uniform gas distribution sets in tension in the sheet material; this results in weakening of this material.

Theories and correlations on several aspects of the fluid bed have been well developed during the last fifteen years and their application in design and construction of equipment for the petroleum, chemical and other industries have been greatly intensified. Nevertheless, the major aspects, such as (*i*) bubble and slug formation, (*ii*) heat transfer, and (*iii*) scaling up of models, have not been fully explored. A greater success of the fluid bed technique in the textile and paper industries as well as in other industries wherein it has been already in use would depend on a comprehensive knowledge of these aspects. These are discussed in some detail below.

Bubble Phenomenon

In dense-phase gas-solid fluid beds, bubbles of gas are usually observed to form in the region above the false bottom and traverse erratically along the bed height. These bubbles are further observed to coalesce and grow during their upward motion. The formation, coalescence and growth

of bubbles, therefore, appears as one of the phenomena inherently associated with dense-phase fluid beds. But it also appears that a non-bubbling state can exist.

As the mass velocity of the fluidizing medium is increased over that required for incipient fluidization, a gas-solid fluid bed essentially becomes unstable causing disuniformity in the fluidized state. Under such conditions a part of the gas flows as bubbles while the remainder takes care of fluidization.

Bubble characteristics of a fluid bed are as follow:

1. Uniformity of the bed is retained at incipient fluidization and there is considerable support for this view[18,19]. But it is least likely to be valid just near the false bottom[20] or at mass velocities greater than that required for incipient fluidization.

2. The gas bubbles rising from the bottom of the bed grow in size as a result of bubble coalescence and decreasing pressure of gas along the height of the bed[21].

3. It has been established that the velocity of rise of a bubble is a function of its volume and is given by the expression, $U=0{\cdot}792\ g^{\frac{1}{2}}\ V^{\frac{1}{3}}$, where U is the velocity, g is the acceleration due to gravity, and V is the volume. This relation was formerly confined to bed diameters of 3 and 6 in., but it has been found to hold good for bubbles rising in a bed of 2 ft square. The experimental results of Davidson and coworkers[22] on the rate of rise of bubbles in fluid beds have shown close agreement with the semi-empirical relation of Davies and Taylor[23] developed for gas bubbles rising in an inviscid liquid.

The nature and mode of propagation of bubbles in fluid beds is still a subject of controversy. But it is known that a bubble is unstable and would tend to rupture when its size is greater than the critical size. It can, therefore, be anticipated that when the maximum size of these bubbles is of the order of the particle size, the bed will behave as a homogeneous phase and the fluidization will remain smooth. The main factors which determine the bubble size are (*i*) size of solid particles in use, (*ii*) gas-solid density difference, and (*iii*) viscosity of the fluid.

Heat Transfer Rates

Heat transfer in fluid beds can take place in three ways, viz. transfer between (*i*) wall and bed, (*ii*) internal surfaces, and (*iii*) bed particles. Heat transfer rates between wall and internal surfaces are found to be similar. Most of the theoretical and experimental work in this direction pertains to the first two. However, the dependency of the heat transfer coefficient on innumerable variables made theoretical work most difficult and the hypotheses[24–27] put forward so far give no satisfactory treatment of the mechanism except that they indicate the relative importance of certain variables like fluid mass velocity. These hypotheses suggest that the core of the fluid bed

is constant. Heat transfer is believed to take place through a boundary layer made up of the gas and solid particles. Though the fluid bed drier has been found to be suitable in textile processing, little is known of the mechanism of heat transfer to textile or like materials in fluid beds.

The experimental data available in literature pertain to beds within 6 in. diam. with the single exception of data of Vreedenberg[28]. Hence, either the application of the empirical correlations outside the range of experimental data published or use of heat transfer coefficients available in literature is likely to mislead design calculations of large-scale fluid bed equipment. Under such circumstances, the only reliable method seems to be an experimental determination of the heat transfer coefficient under desired conditions.

Scaling up of Models

A chemical process which is initially developed in the laboratory passes through a number of stages before it takes the form of a full scale plant for commercial production. The number of stages varies from one process to the other. However, it is broadly divided into the following three stages: (*i*) laboratory scale, (*ii*) pilot plant, and (*iii*) full scale (commercial size plant). In general, the above three stages are followed in succession in order to translate the laboratory scale process into a commercial size plant. While doing so, the principles of scaling up of models are considered and strictly applied. For fluidized systems, these considerations also apply but with the present state of knowledge on bubble formation and heat transfer mechanism in fluid beds it is not possible to scale up fluid bed equipments on theoretical considerations alone. Consequently, only trial-and-error methods have been adopted so far. Similarly, data on distribution of gas to fluid beds are meagre. Some of the methods of gas distribution and elimination of bubbles that are employed for design purposes are presented below.

Experimental work on fluid beds indicates that the effectiveness of gas distribution at bed entrance is limited to the region of the false bottom; and it is reported in literature that smoother fluidization is possible in shallow beds by using sintered plate false bottoms. But, for deep beds where smooth fluidization is desired, the design of gas distribution system is a matter of trial and error. However, disintegration of large bubbles in a fluid bed is accomplished either by supplementary gas supply or by providing a pulsating gas current into the bed.

SUMMARY

The term fluidization refers to a certain mode of contacting solids with fluids. Terms such as incipient fluidization, expanding and moving bed signify the various phases of fluidized particles.

Fluid bed science is about two decades old and owes its origin to the petroleum industry. The fluidization bed technique is employed in almost all vapour phase catalytic reactions. It has also been employed in accomplishing limestone calcination, roasting of iron and gold ores, manufacture of carbon black, production of water gas, coal gasification and nuclear reactor construction. The latest application of the fluid bed principle has been in the textile and paper industries.

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Use of some basic Heat Transfer Concepts in stepping up Production from a Sulphuric Acid Plant

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Taking the contact sulphuric acid plant as an example, it is shown how increased production beyond rated production can be obtained from an existing plant by the use of some fundamental heat transfer concepts related to velocity and temperature differences. Though the discussion is specifically for a sulphuric acid plant, it is hoped that the ideas put forth would be useful in other chemical plants also, as the unit operation of heat transfer forms a controlling part of most chemical plants.

Normally most chemical plants have an inherent built-in over-capacity (usually 5–10 per cent of the rated capacity) which can be tapped quite easily. But, sometimes, it is found necessary to achieve production rates beyond this limit. Every production engineer in charge of a chemical plant must, at one time or the other, face the problem of getting from the plant production beyond its rated design capacity. In case the increased capacity required is appreciable, there is no alternative but to instal a plant for the additional capacity. However, if the increase in capacity required beyond the overdesign limit is small, say 5–10 per cent, and if the increase is not required over a very long period, it may be worthwhile, and in some cases possible, to increase the production somewhat by a calculated change in the operating conditions without making major modifications in the existing plant and equipment. A thorough study of the various factors involved is required for achieving the increased production in this way. This study has been made in the light of the authors' experience by choosing as example the contact sulphuric acid plant with a maximum design capacity of 50 long tons/day of 100 per cent acid. As in most chemical plants, in the sulphuric acid plant also, the unit operation of heat transfer plays a very important role, and the heat exchange equipment may be one of the major bottlenecks in the way of getting increased production. A few of such possible bottlenecks along with ways and means of overcoming them are discussed in this paper. There are some changes, like addition of extra catalyst in the converters, which must be effected in order to achieve in-

creased production. Also it is assumed that the main air blower has usually a margin for being operated at higher discharge pressures

BASIC CONCEPTS

The basic relationship governing heat transfer in any heat exchange equipment, be it a boiler, economizer or heat exchanger of any kind, is represented by the following equation:

$$Q = UA\triangle T_m$$

where Q = quantity of heat transferred, B.t.u./hr;
U = overall heat transfer coefficient, B.t.u./(hr) (sq.ft) (°F.);
A = heat transfer area; and
$\triangle T_m$ = mean temperature difference between the hot and the cold media.

In a plant the heat transfer area of the heat exchange equipment is fixed. Therefore, for any increase in production from the plant, the heat transferred (heat duty) in any particular equipment can be increased by increasing either U or $\triangle T_m$, or both.

Increasing U. The overall heat transfer coefficient is composed of individual film heat transfer coefficients; and increase in the film coefficients results in an increase in the overall coefficient. The film coefficients are dependent on the velocity of flow in addition to other variables.

The relationship can be expressed as:

$$h \propto cv^n$$

where h = film coefficient of heat transfer, B.t.u./(hr) (sq.ft) (°F.);
v = velocity, ft/sec.; and
c and n = constants depending on the system and on the geometrical configuration of the equipment; for tube side, n=0·8.

It is apparent from the relationship that the film coefficient can be increased by increasing the velocity of flow, though the exact magnitude of the increase will be determined by the constants c and n which are dependent on the system and the geometrical configuration.

Increasing $\triangle T_m$ ⊙ The mean temperature difference between the hot and cold streams can be increased by altering the stream inlet temperatures to the heat exchange equipment. This can be done only if the process allows such a change. Also in some cases it may be possible to increase $\triangle T_m$ by switching from parallel flow to countercurrent or cross flow, but normally most of the heat exchange equipment is already designed for countercurrent or cross flow.

HEAT EXCHANGE EQUIPMENT IN SULPHURIC ACID PLANT

In a contact sulphuric acid plant, the following are the main items of heat exchange equipment: (*i*) waste heat boiler, (*ii*) gas-to-air heat exchanger for cooling of converted gases, and (*iii*) acid coolers.

These three equipment are discussed below, in detail, with respect to the use of the above heat transfer fundamentals in increasing their heat duty and thus helping in increasing the plant production.

Waste Heat Boiler. In most modern contact sulphuric acid plants a waste heat boiler, either of the flue-tube type or of the water-tube type, is invariably provided after the sulphur burner to recover heat (and generate by-product steam) from the burner gas. Since the boiler is a major imported component of the plant it is important to be able to boost up the duty of the boiler.

Let us take, for example, a practical case of a flue-tube boiler designed for working steam pressure of 225 p.s.i.g. (saturated) to cool the gases from the sulphur burner at an acid production rate of 50 tons/day (678·5 lb. moles/hr of gases containing 7·34% SO_2) from a temperature of 837°C. to 420°C. with a gas-side pressure drop of 3·89 in. W.G. It is desired to operate the plant at 60 tons/day acid production. There are two alternative methods of operation available for effecting this increase in production:

(*i*) By keeping the same concentration (7·34% SO_2) and therefore same temperature (837°C.) but by correspondingly increasing the volume of the sulphur burner exit gases (812 lb. moles/hr). This will be achieved by burning the sulphur required for 60 tons/day acid production with an increased amount of air, giving 7·34 per cent SO_2 concentration and a gas temperature of 837°C.

(*ii*) By burning the sulphur required for 60 tons/day acid production with the same amount of air as used for 50 tons/day acid production, giving the same amount of gases as for 50 tons/day production (678·5 lb. moles/hr) but at increased concentration (8·7% SO_2) and temperature (980°C.). Actually, even though the lb. moles/hr of gas produced in this case at 60 tons production will be the same as at 50 tons/day production, the volume rate will be somewhat larger due to the increased temperature. The concentration of the gas can be reduced after the boiler (either just before the converter or at intermediate stages) by dilution with air.

In case of a boiler, since the film coefficient on the boiling water side is much higher than on the gas side, the gas film coefficient is controlling and therefore approximately:

$$U = h_{gas}$$

In case of the first alternative the heat transfer possible in the boiler will increase only due to the increased flow velocity (there is no increase in $\triangle T_m$):

$$\frac{Q_{60}}{Q_{50}} = \frac{U_{60}}{U_{50}} = \frac{h_{60}}{h_{50}} = \left[\frac{812}{678{\cdot}5}\right]^{0{\cdot}8} = 1{\cdot}157$$

Therefore, only an increase of 15·7 per cent is possible. This means that the boiler will not be able to cope with the increased heat duty for 60 tons production, if this alternative is used (i.e. the temperature of the boiler outlet gas will not come down to the required 420°C.). Also since the pressure drop is dependent mainly on the velocity, it is estimated that the gas-side pressure drop across the boiler will increase from 3·89 in. W.G. to 5·5 in. W.G. (i.e. about 42 per cent).

However, in case of the second alternative, the heat transfer possible in the boiler will increase more due to the increased $\triangle T_m$ than due to the slight flow velocity increase resulting from higher average gas temperature in the boiler. In this case:

Average gas temperature at

60 tons production $= \dfrac{980+420}{2} = 700°\text{C.}$

Average gas temperature at

50 tons production $= \dfrac{837+420}{2} = 629°\text{C.}$

$\triangle T_m$ at 60 tons production $= \dfrac{(980-203)-(420-203)}{2{\cdot}303 \log\left(\dfrac{980-203}{420-203}\right)} = 439°\text{C.}$

$\triangle T_m$ at 50 tons production $= 389°\text{C.}$

Since in case of this alternative the increased heat transfer is both due to the increase in U (resulting from volume rate increase) and the increase in $\triangle T_m$,

$$\frac{Q_{60}}{Q_{50}} = \left[\frac{U_{60}}{U_{50}}\right]\left[\frac{\triangle T_{m60}}{\triangle T_{m50}}\right]$$

$$= \left[\frac{273+700}{273+629}\right]^{0{\cdot}8}\left[\frac{439}{389}\right] = 1{\cdot}207$$

Therefore, an increase of more than 20 per cent in heat duty on the boiler is possible, provided the steam mountings and fittings are adequately oversized (which is usually the case). It is estimated that the gas-side pressure drop across the boiler will increase from 3·89 in. W.G. to only 4·3 in. W.G. (i.e. about 11 per cent).

From a comparison of the two alternatives it is seen that the second alternative of higher concentration and temperature will enable the waste heat boiler to cope with the increased heat load at 60 tons/day acid production with a gas-side pressure drop increase of only 11 per cent. An extension of this reasoning may indicate that even further increase in heat duty should be possible. However, the limitations are the maximum temperatures which can be tolerated in the burner and the steam raising for which the boiler mountings and fittings are suitable.

Gas-to-Air Heat Exchangers. Mostly these heat exchangers in a sulphuric acid plant are designed to use process air for cooling, the heated air being used in the burner. In such a case the gas and air flow rates are nearly the same. Both the air-side velocity and the $\triangle T_m$ can be increased by installing a high-capacity, low-pressure fan for effecting this cooling at least in some of the heat exchangers. The process air has to be heated to some extent before it is let into the sulphur burner in order to avoid sublimation of sulphur. By thus supplying the cooling air from an independent source the heat transfer in an existing heat exchanger can be increased considerably. The heated air can either be used somewhere else or can be vented to the atmosphere. In the latter case this will result in the loss of heat, but this may not be undesirable if the heat exchanger is proving as a bottleneck in the way of increasing the production.

Acid Coolers. In the case of acid coolers, the hot acid temperature is fixed by the process. The cooling water temperature is also usually fixed. Therefore, it is normally not possible to increase $\triangle T_m$ unless there is a margin in the cooling tower operation and lower cooling water temperatures are possible. The increase in heat transfer effected by the increased flow velocity will not be adequate to cope with the increased heat duty at the increased production, as in the case of the first alternative for waste heat boiler. It is therefore necessary to add a few rows of cooler pipes for increased production.

CONCLUSION

The basic heat transfer fundamentals are reviewed to determine the means of increasing the heat transfer in an existing heat exchange equipment. These are applied to the various heat exchange equipment in a contact sulphuric acid plant (namely, waste heat boiler, gas-to-air heat exchangers and acid coolers) to see how they can be made to take up increased heat loads if the acid production is to be increased somewhat.

It is seen that the waste heat boiler may be made to take up considerably increased heat loads by operating the sulphur burner at higher concentrations and temperatures due to resulting increase in temperature difference and velocity. In this way the increase in gas-side pressure drop across the boiler will also not be excessive. However, there are other limita-

tions which must be kept in view when effecting an increase in production from the existing plant.

It must be pointed out that any such increase in production from an existing plant beyond its design capacity must be temporary, because increasing the production over a long period will be a strain on the plant and may reduce its life.

Though the discussion given in this paper is specifically for a sulphuric acid plant, the ideas put forth would be found useful in other chemical plants also where the unit operation of heat transfer plays an important role.

Work Efficiency in Alcohol Distillation

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The distillery operation referred to in this paper is for the production of ethyl alcohol from molasses. There are essentially two steps in the distillery operation, namely, production of rectified spirit from weak molasses wash and the final distillation of rectified spirit to absolute alcohol. From the thermodynamic point of view, distillery operation is relatively an inefficient process resulting in sizeable steam consumption and increase in the cost of finished product. It has been shown that a thermodynamic efficiency of 81 per cent can be achieved in the distillation of 8-10 per cent alcohol to 95 per cent (by wt). In actual practice, however, the efficiency of distillation varies from 40 to 70 per cent depending upon the design of distillery and operating conditions.

One of the methods of separation of two or more volatile liquids into their components is by distillation. One of the distillation operations, which is of rather prime importance for our industry, is the separation of ethyl alcohol from the dilute wash obtained from the fermentation of molasses. In recent years, there has been a tremendous increase in the installed and production capacity of alcohol distilleries and hence a review of the ways and means of increasing their efficiency is opportune. Though ways and means of increasing the efficiency of distillation are well known in theory, yet how far they are of practical consequence needs further study. It is the purpose of this paper to examine the problem of thermal work efficiency in a distillation operation for producing absolute alcohol. To analyse this efficiency, basically three questions have to be considered. These are:

(1) What is the work or heat required theoretically for separating ethyl alcohol from a weak solution and how does this compare with actual figures ?

(2) What are the causes of inefficiency in the operation, if inefficiency is observed in practice ?

(3) How can the operation be improved and its efficiency enhanced at minimum cost ?

THEORETICAL HEAT REQUIREMENT

Heating and cooling are the main operations involved in separation of ethanol from its dilute solution in water and account for the major cost of distillation. Heating is accomplished in the form of open or closed steam at the bottom of various distillation columns and cooling is accomplished

in the condensers primarily by the circulation of cold water to produce the necessary reflux and product.

Thermodynamic Work

From the strictly thermodynamic point of view the work of separation is dependent upon the composition and condition of feed, product and waste streams. Besides these, it is also a function of deviation of the system from an ideal solution and this is represented by activity coefficient. Thus for example, the thermodynamic work of separating a solution of 7·5 per cent (by wt) alcohol at 173°F. into pure alcohol and water at the same temperature can be readily calculated from the following equation:

$$\triangle F = -RT\frac{(X_{1d})}{(X_1)M_d}\Big[\{X_1\log_e\gamma_1X_1+X_2\log_e\gamma_2X_2\}- D\{X_{1d}\log_e\gamma_{1d}X_{1d}+X_{2d}\log_e\gamma_{2d}X_{2d}\} - W\{X_{1w}\log_e\gamma_{1w}X_{1w}+X_{2w}\log_e\gamma_{2w}X_{2w}\}\Big]$$

where $\triangle F$=minimum work (B.t.u./lb. of product).

On substituting the proper values* in the above equation the minimum work requirement comes to 95·5 B.t.u./lb. of absolute alcohol produced. By a similar calculation it is possible to evaluate the work required in various stages of distillation operation. The results are summarized in Table 1.

TABLE 1—WORK REQUIREMENT AT VARIOUS STAGES OF DISTILLATION OF ALCOHOL SOLUTION

	Separation of alcohol		Work *B.t.u./lb. of absolute alcohol*	Requirement of 5 p.s.i.g. steam *lb./Imp. gal. of absolute alcohol*†
	from % (by wt)	to % (by wt)		
Beer and rectification column	7·5	95	88·5	14·6
Dehydration column	95	100	7·0	1·1
Total			95·5	15·7

† Given as the work requirement in terms of steam consumption in the distillation and assumes that: (*i*) total theoretical work is supplied by steam only (this is not quite true because in an actual operation some work is needed to pump cooling water, but for comparison a consistent basis has been chosen); (*ii*) only latent heat of steam is utilized, and (*iii*) 1 gal. of distillate=8 lb.

*The values of activity coefficients have been calculated from the Van Laar correlation, taking the values of the constants *A* and *B* as 7·0 and 7·96 respectively.

Thermodynamic Efficiency

It is not possible to carry out distillation to conform to the values given by theoretical thermodynamic calculations. It is interesting and necessary to know the thermodynamic efficiency by evaluating the work requirement under the best possible actual operation which may or may not be economical in practice. For actual operation, besides the factors mentioned previously, the sink temperature and reflux ratio are the two additional considerations (the sink temperature is the temperature at which any amount of heat can be rejected without any appreciable alteration in its temperature). In this case, the temperature is that of cooling water, say 90°F. It is well known that the lower the reflux ratio, the lower is the work or equivalent steam required for the separation process. This lower limit of reflux ratio is determined by the equilibrium properties of the system and by practical consideration of capital investment in columns, since the number of plates in a column increases with the reduction in reflux ratio. In case of ethanol-water system, the equilibrium properties at 1 atm. are a little peculiar and are such that it is not possible to reduce the reflux ratio (external) to less than 3·5 without sacrificing the purity of the product. From these considerations, the actual work of separation of 95 per cent alcohol from dilute solution of alcohol (7·5 per cent) is calculated as 105 B.t.u./lb. of anhydrous alcohol and quantity of heat requirement as steam at 5 p.s.i.g. per gal. of product works out to 17·4 lb. This gives an overall thermodynamic efficiency of 84 per cent. The thermodynamic efficiency in this particular case decreases with the increase in feed composition of solution as is shown in Fig. 1 by the increase in crossed area ABC which is a representation of inefficiency. Also, it is to be noted that these efficiencies have been considered at a feed temperature of 173°F. and any decrease in feed temperature will bring down the corresponding efficiency figures.

Practical Efficiency

Thermodynamic efficiency is of theoretical importance only and it is, therefore, necessary to define what is called practical efficiency. Practical efficiency is the ratio of work required for separation under the best possible actual operation to the real work required in a distillation operation for producing alcohol. Thus, if the equivalent steam consumption for producing absolute alcohol is 40 lb./gal. of absolute alcohol, then from the figures evaluated above, practical efficiency is equivalent to 47 per cent. The equivalent steam corresponding to the total work requirement in almost all units varies from 30 to 48 lb. steam per gal. of absolute alcohol. Thus, it can be concluded that the present practical efficiency of distillation operation is in the range of 38–62 per cent on the above basis.

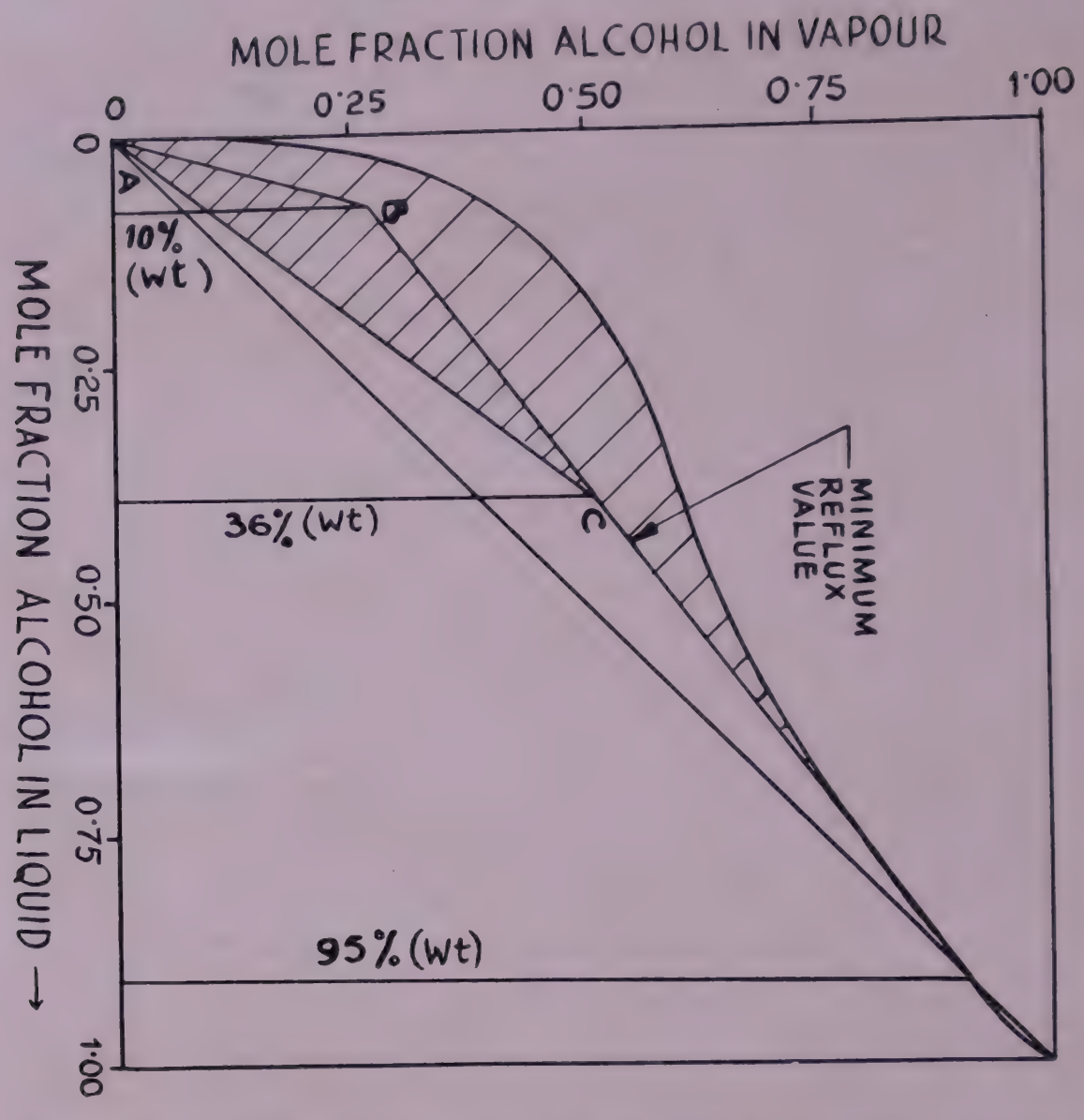

FIG. 1—PLOT OF MOLE FRACTION OF ALCOHOL IN LIQUID VERSUS MOLE FRACTION OF ALCOHOL IN VAPOUR

CAUSES OF INEFFICIENCY IN DISTILLATION OPERATION

It can be seen from the foregoing that considerable scope for increasing efficiency in distillation operation exists and, therefore, the various causes to which inefficiency is attributable are enumerated below.

Rejection of Heat. A given quantity of heat can be made to do useful work by passing this through a turbine or a heat engine. The maximum available work will be limited by the temperature of heat source and the temperature of sink and their respective entropies. In a distillation operation heat is rejected at many places, for example, in vapour condensing against cooling water or disposal of hot waste lees from the bottom of column in the drain or from the condensate if closed steam is used. The heat contained in various streams, if not utilized or is not available for doing some useful

work, will contribute to the inefficiency in the process. Thus, the quantity of heat and the temperature at which it is rejected, are the two important factors to be closely watched.

Irreversibility in Distillation Column and higher Reflux Ratio. Inefficiency in the distillation process is due to heat transfer taking place at the bottom and top of the column. If this heat transfer is carried out on each plate or in stages, then the efficiency can be improved. Thus, if some heat source is available at a lower temperature than what is required at the still, it can be advantageously used between the still and the feed point. Another point is the reflux ratio. The higher the reflux ratio, the less efficient is the process. In the ethanol-water system the excess steam (%) required over a ratio of 3·5 is given below:

Reflux ratio	*Excess steam* %
3·5	—
4·0	11·2
4·5	22·4
5·0	33·6

Low Utilization of available Heat in Steam for the Separation Process. The major fraction of the heat in the steam used is consumed in the heat transfer process rather than for the actual distillation. Thus, for example, when low pressure steam is available at 228°F. and the condenser is running on an average at 95°F., then the net available work in the distillation process is only about 19·5 per cent of total work supplied to the still. These inefficiencies are inherent, but can be reduced if it is possible to utilize some of the process streams advantageously for heating and condensing purposes.

Poor Insulation of various Equipment causing Heat Losses. This is another source of inefficiency due to surface radiation.

HOW THE DISTILLATION OPERATION CAN BE IMPROVED

Numerous suggestions have been made for reducing the inefficiencies of distillation operation and most of these aim at better heat transfer operation like the use of multi-distillation columns working at different pressures, use of vacuum or a combination of such systems. In the case of production of anhydrous alcohol from 95 per cent product the use of glycerine or ether in place of benzene has been suggested to reduce steam consumption in the dehydration column. It is very true that all these methods, if implemented, can contribute to the efficiency of distillation operation but a very careful

study is needed to see if these schemes are economically sound and convenient from the point of view of operation. By limiting the study to the conventional distillation operation as practised in India, the authors strongly believe that there is considerable scope for modifying the present methods of distillation at atmospheric pressure to bring down steam consumption to as low as 24–25 lb. per gal. of anhydrous alcohol.

Hence, practical suggestions are given below. Some of them might be known to many but these are being highlighted on the basis of experience gained in actual operation.

Utilization of waste Heat

(i) **Waste Lees from the bottom of Beer and Exhaust Column.** For every 100 gal. of anhydrous alcohol produced, 1·2 million B.t.u. of heat are available in the form of waste liquid stream from the bottom of beer and exhaust column (availability of heat by cooling to 90°F.; and is different from maximum work available). It is practical to utilize 27–30 per cent of this heat for the cold feed heating and 12–14 per cent can be recovered as a low pressure steam by flashing and recovering the vapours by thermo-compression system. As long as high pressure steam is used anywhere in the system, this thermo-compression will be an economical proposition. This installation, which is simple, has also been proved to be feasible.

(ii) **Waste Heat from Vapours of Rectifying Column.** Almost an equal quantity of heat which is supplied in the reboiler is available in the vapours from the rectification column, though at a lower level of temperature. However, this can be advantageously used for heating the fresh feed before charging it into beer column through the lees heat exchanger. The heat exchanger could be multi-pass type. The temperature and pressure of the balance of unutilized heat are so low that it has to be rejected to water unless a vapour compression system is used.

Maintenance of proper Reflux Ratio in Rectifying Column

It is practical to maintain a reflux ratio very close to 3·5, almost the minimum which is possible in the production of 95 per cent alcohol, at atmospheric pressure. To achieve the conditions of desirable reflux ratio and heat exchanging system, it is imperative to install the necessary indicating and recording type instruments to measure reflux, concentration, flow and temperature conditions.

Utilization of Heat in Vapours from Beer Column

The vapours available from the beer column are at 200–203°F., while the bottoms of dehydration columns work at about 173°F. Thus, one of the most practical ways to save heat is to utilize the vapours from beer column in a partial condenser to boil the bottoms of the dehydration column.

The vapours from partial condenser, richer in alcohol, are then fed to the rectification column and the liquid from the partial condenser is sent to the exhaust column. It is possible to save approximately 40–45 per cent of the steam requirement in the dehydration column. Any effort to save additional steam over this in the dehydration column will result in corresponding increase in steam consumption in the exhaust column. This is simply due to the limitation of exhaust column to handle liquid from the partial condenser beyond a certain concentration and quantity without any increase in the steam consumption.

Indirect Savings

(i) **Useful Work of high Pressure Steam.** In case the generation of steam in a distillery is of the order of 150 p.s.i.g., then it is economical to use a heat engine turbine to recover power and then to utilize the 7–8 p.s.i.g. exhaust steam in operation. This high pressure steam can also be used to compress the low pressure flash steam to recover the heat from the waste lees of distillation columns.

(ii) **Lagging.** Proper lagging of steam, vapour lines and distillation columns is an important factor. The losses due to improper lagging can be as high as 7–10 per cent of heat requirements.

(iii) **Use of Electric Pumps in Place of Steam Pumps.** In case extra power is available from the expansion engine or otherwise, it may be beneficial to use electric pump in place of low efficiency steam pump for pumping molasses.

(iv) Return of all condensate from closed steam supply to the distillery boiler is desirable.

The possible practical figures of steam consumption at each stage in different columns are given below:

Stages	Steam (5 p.s.i.g.) consumption *lb./gal.*
Beer column ..	17
Exhaust column ..	2
Dehydration column ..	6
Total ..	25

SUMMARY AND CONCLUSION

The heat or steam requirements in distillation operation form a major and important part of the total cost. The comparison, on consistent basis, of theoretical calculations and the average practical steam figure gives a practical efficiency between 38 and 62 per cent.

The causes of inefficiencies have been reviewed and it is shown that by implementing a few simple but useful suggestions, it is possible to achieve economically a total steam consumption of 25 lb./gal. of absolute alcohol, corresponding to a practical efficiency of 73 per cent.

This efficiency can still be improved by considering a system radically different from the one which employs the conventional atmospheric distillation towers, but this will be the subject of a future article. It may be added in this context that the efficiency figures may have no absolute significance, but these do give a comparative idea of distillation operation in practice and theory and suggest the limitation on the work and steam requirements. As is the case in any other production plant, the importance of accurate design and proper operational control cannot be minimized.

Nomenclature

F = Minimum work of separation (free energy charge) per mole of mixture
R = Gas law constant
T = Absolute temperature
X_1 = Mole fraction of alcohol in mixture
X_2 = Mole fraction of water in mixture
γ_1, γ_2 = Activity coefficients of two components
D = Moles of top product per mole of feed
W = Moles of bottom product per mole of feed
M_d = Molecular weight of the product
d, w = Subscripts referring to distillate and bottoms respectively

AUTHOR INDEX

Bhat, T. R. 36
Bilimoria, M. H. 47
Bishnoi, P. R. 1

Chandiramani, K. R. D. .. 22
Chandrasekaran, P. .. 129
Chaudhuri, Sh. S. K. 185

Datta, R. L. .. 32, 111
Deshpande, D. D. 10
D'Mello, J. I. 167

Gandhi, P. N. 138
Gokhale, K. S. 160
Gokhale, Y. W. 36
Gupta, R. K. 135

Ibrahim, S. H. 17

Kalbag, S. S. 167
Kalyanam, N. 94
Kalyanasundaram, C. V. .. 32
Kapur, J. P. 191
Krishna, B. H. 167
Kuloor, N. R. 17
Kumar, R. .. 32, 111

Laddha, G. S. 129
Lakshminarayana, S. K. .. 167

Mathur, B. S. 36
Mohan Rao, N. A. 171
Mukhopadhyay, S. S. .. 7

Narasimhan, G. 125

Pabbi, V. R. 191
Parihar, D. B. 22

Ramachandra, B. S. 167
Rama Char, T. L. 153
Ramanathan, P. K. 167
Ramaswamy, S. 94
Rao, M. N. 58

Saha, A. N. 7
Sarma, K. J. R. 58
Sastry, V. S. 36
Satapathy, R. 180
Saxena, P. K. 22
Sen, P. 58
Sen Gupta, P. 58
Shah, K. H. 1
Sharma, M. M. 1
Shukla, K. K. 22
Subrahmanyan, V. 167
Subramaniam, M. 111
Sundaram, R. 10
Sundararajan, J. 153

Vasudev Rao, M. N. 167
Venugopal, B. 17

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